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DESIGN AND EVALUATION OF DIMETHYL CARBONATE PRODUCTION FROM CARBON DIOXIDE

Mr. Pichayapan Kongpanna

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By	Mr. Pichayapan Kongpanna
Field of Study	Chemical Engineering
Thesis Advisor	Professor Suttichai Assabumrungrat, Ph.D.
Thesis Co-Advisor	Professor Rafiqul Gani, Ph.D. Associate Professor Varong Pavarajarn, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Doctoral Degree

....Dean of the Faculty of Engineering
(Professor Bundhit Eua-arporn, Ph.D.)

THESIS COMMITTEE

....Chairman
(Associate Professor Tawatchai Charinpanitkul, D.Eng.)
....Thesis Advisor
(Professor Suttichai Assabumrungrat, Ph.D.)
....Thesis Co-Advisor
(Professor Rafiqul Gani, Ph.D.)
....Thesis Co-Advisor
(Associate Professor Varong Pavarajarn, Ph.D.)
....Examiner
(Assistant Professor Amornchai Arpornwichanop, D.Eng.)
....Examiner
(Dr. Palang Bumroongsakulsawat, Ph.D.)
....External Examiner
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งานวิจัยนี้เสนอกรอบแนวทางการสังเคราะห์กระบวนการทางวิศวกรรมเคมีโดยใช้คอมพิวเตอร์เข้ามาช่วยเหลือเพื่อให้ได้กระบวนการที่มีความยั่งยืนมากยิ่งขึ้น โดยกรอบแนวทางนี้มีการรวมวิธีการ เครื่องมือ หลักการและฐานข้อมูล โดยแบ่งออกเป็นขั้นตอนการสังเคราะห์ การออกแบบ และนวัตกรรม ในขั้นตอนการสังเคราะห์โครงข่ายเพื่อหากระบวนการที่เหมาะสม ขั้นตอนการออกแบบรวมถึงการคัดเลือกและวิเคราะห์กระบวนการพื้นฐาน ทางด้านความเป็นไปได้ในการดำเนินการ เศรษฐศาสตร์ วงจรวัฏจักรชีวิต และค่าความยั่งยืน ซึ่งถูกใช้เป็นเป้าหมายในขั้นนวัตกรรม ซึ่งประกอบไปด้วยการสร้างและคัดเลือกกระบวนการที่มีความยั่งยืนยิ่งขึ้น โดยใช้ทฤษฎีปรากฏการณ์ ซึ่งกรอบแนวทางที่ได้นำเสนอนี้ได้นำไปประยุกต์ใช้กับการออกแบบกระบวนการผลิตไดเมทิลคาร์บอเนตจากคาร์บอนไดออกไซด์ โดยกระบวนการผลิตไดเมทิลคาร์บอเนตในโครงสร้างขนาดใหญ่มีการใช้คาร์บอนไดออกไซด์ทั้งวิธีทางตรง และวิธีทางอ้อมซึ่งประกอบไปด้วยการผลิตผ่าน ยูเรีย เอทิลีนคาร์บอเนต และโพรพิลีนคาร์บอเนต ซึ่งได้ถูกสร้างและประเมินเพื่อหากระบวนการที่ผ่านการคัดเลือก และนำไปวิเคราะห์เพื่อหาทางพัฒนา โดยใช้ทฤษฎีปรากฏการณ์ เพื่อให้ได้กระบวนการที่ดีและยั่งยืนยิ่งขึ้น บนตัวชี้วัดทางด้านต่างๆ ได้แก่ ความยั่งยืน เศรษฐศาสตร์ และวงจรวัฏจักรชีวิต พบว่ากระบวนการผลิตไดเมทิลคาร์บอเนตจากยูเรียโดยใช้หอกลั่นที่มีปฏิกิริยาเป็นกระบวนการทางเลือกที่ดีที่สุด และแสดงผลลัพธ์ของตัวชี้วัดที่ดีกว่ากระบวนการผลิตของบายเยอร์

ภาควิชา วิศวกรรมเคมี
สาขาวิชา วิศวกรรมเคมี
ปีการศึกษา 2558

ลายมือชื่อนิสิต ....
ลายมือชื่อ อ.ที่ปรึกษาหลัก ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....
ลายมือชื่อ อ.ที่ปรึกษาร่วม ....

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PICHAYAPAN KONGPANNA: DESIGN AND EVALUATION OF DIMETHYL CARBONATE PRODUCTION FROM CARBON DIOXIDE. ADVISOR: PROF. SUTTICHAI ASSABUMRUNGRAT, Ph.D., CO-ADVISOR: PROF. RAFIQUL GANI, Ph.D., ASSOC. PROF. VARONG PAVARAJARN, Ph.D., 266 pp.

A systematic computer-aided framework for sustainable process design is presented. The framework integrated with various methods, tools, algorithms and databases is based on a combined process synthesis-design-intensification method. The synthesis-stage involves superstructure based optimization to identify promising networks. The design-stage involves selection and analysis of the identified networks as a base case design in terms of operational feasibility, economics, life cycle assessment factors and sustainability measures, which are employed to establish targets for improvement in the next-stage. The innovation-stage involves generation and screening of the more sustainable alternatives through a phenomena-based process intensification method. The proposed framework was applied to the CO_2-based DMC production process. A superstructure of processing routes including CO_2 direct synthesis and indirect syntheses via urea, ethylene carbonate and propylene carbonate, was generated and evaluated to determine the most promising processing route, which was then analyzed in detail to identify design improvement targets. Through a phenomena-based method, new more sustainable process alternatives matching the design improvement targets were identified. For the evaluation of alternatives, the measures include sustainability metrics, economic potential indicators as well as LCA factors. The urea route with reactive distillation was found to be the best alternative, offering superior performance to the conventional BAYER process.

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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		Co-Advisor's Signature	....

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CHAPTER I
INTRODUCTION

1.1 Rationale

In the past decades, there have been increasing concerns and therefore, more attention on global warming and emission of gases such as methane (CH_4), nitrogen dioxide (N_2O), chlorofluorocarbon (CFC) and carbon dioxide (CO_2), which are considered to be greenhouse gases (GHGs) because of their contribution to global warming. Since the beginning of the industrial revolution around 1850, the average atmospheric concentration of CO_2 has increased from 280 ppm in 1850 to 370 ppm currently and as a result, the average global temperature has increased by between 0.6 ˚C - 1 ˚C during this period (Stewart *et al*., 2005). The use of fossil fuel systems such as coal-fired power plants are regarded as one of the major sources of CO_2 emissions, which accounts for about 33–40% of the total anthropogenic emissions of carbon worldwide (Xu *et al*., 2008). The need for the reduction of the GHGs emissions on a global scale is urgent. Several options may be considered to reduce the effect of GHG, for example, lowering energy consumption by increasing the efficiency of energy utilization, using clean combustion fuels or, using renewable energies, in addition to developing technologies of CO_2 capture, storage, and utilization.

It was reported that the CO_2 emissions from the petrochemical sector, for example, oil refineries, LNG sweetening, ammonia, ethane and other petrochemical process and ethylene oxide to atmosphere are estimated around 1460 $MtCO_2$/yr, while, CO_2 utilization in chemical process such as urea, methanol, dimethyl ether, tert-butyl methyl ether (TBME) and organic carbonate is estimated only around 178 $MtCO_2$/yr (Aresta *et al*., 2013). Although, no single solution will be sufficient in reducing this large net CO_2 emission, a potential strategy could be to more utilize CO_2 as a chemical feedstock for conversion to more valuable chemicals (Centi *et al*., 2009). In recent years, the transformation of CO_2 to valuable chemicals has attracted much attention (Dai *et al*., 2009). Many researchers have investigated CO_2 utilization in various reactions such as CO_2 based hydrogenation to methanol, CO_2 based cycloaddition to epoxides, CO_2 based carbonylation of amines or alcohols to carbonate compounds, and, CO_2 based reduction under photo-irradiation or electrolytic conditions. An interesting option is the production of organic carbonates, which can be roughly categorized into cyclic and linear carbonates, such as ethylene carbonate (EC), propylene carbonate (PC) and dimethyl carbonate (DMC). With rising demand for organic carbonates, the feasibility of CO_2 based reaction to produce them becomes an interesting and more sustainable choice.

This work focuses on the evaluation of the production of dimethyl carbonate (DMC) by several reaction routes. DMC is an important carbonylating and methylating reagent used in various fields such as medicine, pesticides, composite materials, flavoring agent and electronic chemicals (Omae, 2013; Pacheco *et al*., 1997). PERP (process evaluation/research planning) program in 2012 (CHEMSYSTEMS, 2012) has reported that the potential demand for DMC could be much bigger. DMC is currently used as intermediate (51% of production of DMC) in polycarbonate production. The global future potential uses of DMC are as a possible fuel additive and as an intermediated in the manufacture of isocyanates (which are used to make polyurethane foams). DMC's possible use as gasoline blending component is due to its very high oxygen containing (53 wt.% of O_2), good blending octane, freedom to phase separation, good solvent, low toxicity and rapid biodegradability. The attention of DMC production is gradually grown up. From Eni polimeri Europa's report (2009), the DMC production process was designed and established the DMC production capacity of 48,300 ton DMC per annum in 1998. In 2004 the total capacity has been increased to 96,600 ton DMC per annum with the start-up of a second unit. The research project from Twente University by Sustronk et al., (2015), indicated the research project dealing with the production of dimethyl carbonate (DMC). The plant was designed to be able to supply DMC as an anti-knocking agent to a large refinery; the plant capacity was 450,000 ton DMC per annum, with a purity of 99.8 wt%.

Although processes for the production of DMC are well-established, for example, BAYER (Kricsfalussy *et al*., 1996), UBE (Matsuzaki *et al*., 1997) and ENIChem (Tundo *et al*., 2002), the synthesis of DMC utilizing CO_2 is an option worth investigating since it offers direct benefits to the environment while creating valuable products from the emitted and undesired CO_2. In this research, CO_2 based processes for production of DMC are selected for evaluation and compared according to a set of performance criteria that includes yield, energy consumption, CO_2 emission and environment impact indicators. However, it is well known that the utilization of CO_2 for the production of fine chemicals is severely limited by the reaction equilibrium in most cases (Omae *et al.*, 2012). The high stability of CO_2 leads to a very low driving force, which has to be compensated if higher value chemical products are to be produced. It is necessary to first create a full reaction tree of higher value chemicals that can be produced directly or indirectly with CO_2 as a reactant. This requires each synthesis route to be investigated for thermodynamic feasibility and availability of catalysts, when necessary. Having the reaction tree, different synthesis routes can be investigated to find the best set of value-added products by CO_2 utilization and thereby reduction of net CO_2 emission as a first step, the synthesis routes for a selected set of higher value products could be investigated based on known reaction data.

Process synthesis and design plays an important role when developing new technologies, when creating new facilities, or when retrofitting existing production processes. Due to the increasing environmental and economic concerns and governmental policies, chemical and biochemical processing industries need to develop and adopt more environmental friendly as well as technologically and economically competitive solutions. To find optimal and more sustainable solutions, the environmental constraints must be assessed in a comprehensive way, side by side with economic and technical criteria. In the chemical industry improvements related to the use of sustainable methodologies and efficient use of resources are needed in order to achieve reductions in energy consumption, waste generation, environmental impact and cost. The concept of sustainable process design was proposed by many authors. SustainPro proposed by Carvalho et al., (2008) and ENVOPExpert (Halim et al., 2011) are expert systems that, given the information concerning the process in the form of a flowsheet, process chemistry, and material information, can automatically detect the waste components in the process, diagnose the sources of their origin, and suggest intelligent design alternatives (heuristic) to eliminate or minimize them. Process evaluation on life cycle assessment, LCSoft (Kalakul et al., 2014) and

SimaPro (PRé, 2012) are softwares to perform LCA which are used for a variety of applications, like carbon footprint calculation, environmental impact of products or utilities and environmental reporting. Process improvements are typically achieved through an evolutionary approach, where knowledge gained from process understanding together with expert knowledge on process engineering is applied. These methodologies, while very useful, are not generic enough and for their application, a number of additional methods and tools and their related data, are needed. Consequently, using the advances in computer science and computational algorithms for process analysis, it becomes advantageous to employ computer-aided modeling systems and tools for integrated process retrofitting analysis. The limitation with this approach, however, is that new, innovative and more sustainable process designs may not be found because the search space employed is limited in size in the trial and error, experiment-based approaches. The same is true for model-based solution approaches where the models employed have limited application range.

There are needs to develop a methodology for process synthesis-design-intensification to find the best processing route, from among numerous process alternatives, to convert given raw materials to specific (desired) products, subject to pre-defined performance criteria. Hence, process synthesis involves analysis of the problem to be solved, and, generation, evaluation with environmental and economic measures, the performance criteria also considers measures for more sustainable alternatives, such as, energy consumption, net CO_2 emission, raw material depletion and life cycle assessment factors at their targeted levels or better and screening of process alternatives so that the best process option can be identified.

1.2 Objective of the research

The objective of this research is to first, highlight the main features and architecture of the framework for process synthesis-design-intensification where the three-stage decomposition approach has been implemented together with the associated work-flow and data-flow; and second, to highlight the application of the three-stages framework to the synthesis-design of a more sustainable CO_2 utilization based process for DMC production. In this work, in addition to environmental and economic measures, the performance criteria also considers measures for more sustainable alternatives, such as, energy consumption, net CO_2 emission, raw material depletion and life cycle assessment factors at their targeted levels or better.

1.3 Scope of the research

- Establish the systematic framework for process synthesis and design to achieve more sustainable process.
- Apply the proposed framework to the CO_2-based DMC production process. The specification of CO_2 for utilization is set at high purity as feedstock (100 wt.% purity).
- Perform superstructure based optimization of the DMC production processes to identify promising processing networks that convert a given set of raw materials to a desired set of products.
- Identify processing networks as a base case design with steady state simulation, in terms of operational feasibility, economics, life cycle assessment factors and sustainability measures, which are employed to establish targets for improvement in the innovation stage.
- Propose the innovation method of the more sustainable process alternatives through a process intensification method.

1.4 Structure of thesis

This thesis is divided into 7 chapters, starting with introduction, background and motivation of this thesis in Chapter 1. Chapter 2 summarizes the previous researches on CO_2 utilization (based on CO_2 conversion to chemicals) and provides the reviews on the process synthesis–design-intensification. Chapter 3 is the theory that provides the information of systematic methodology, how to synthesize the framework, superstructure, process synthesis and design, process evaluation and process intensification for more sustainable process with the process performance indicators. Chapter 4 highlights methodology for sustainable process design used in this study. The step-by-step methodology and necessary tools are explained.

Chapters 5 and 6 demonstrate the application of the proposed framework by considering a case study on DMC production based on CO_2 utilization. Chapter 5 provides the preliminary evaluation of different CO_2-based processes for dimethyl carbonate production, considering various process performance indicators, e.g. CO_2 emission, atom efficiency, environment and human impacts while Chapter 6 fully applies the proposed methodology to perform the design of sustainable chemical processes for CO_2-utilization network for dimethyl carbonate production. The use of computer-aided tools for solving more complex problem with the optimization processing route from big superstructure, process simulation, process evaluation in economic and life cycle assessment and process intensification with phenomena based synthesis are integrated in this work. Chapter 7 is the conclusion and recommendation section to conclude the thesis results and to provide further suggestions.

CHAPTER II
LITERATURE REVIEW

2.1 CO_2 utilization

Carbon dioxide (CO_2) is a greenhouse gas (GHG) which is a major cause for global warming problem. Recently, there are many efforts from both academic and industrial sectors to propose methods for reduction of the CO_2 emission to the environment. At present, the method to handle CO_2 problem is carbon capture and storage (CCS). There are several drawbacks of this method - CO_2 is not eliminated, and the costs for transportation and capturing methods are often expensive. Consequently, it is advantageous to develop an alternative approach for reducing the CO_2 emissions. In recent years, the transformation of CO_2 to valuable chemicals has attracted much attention (Aresta *et al*., 2013), CO_2 utilization is one of the potential pathways to reduce CO_2 emission and to make valuable products such as methanol, cyclic carbonate compounds and dimethyl carbonate (Dai *et al*., 2009).

Recently, several reviews on carbon dioxide utilization have been published. In 2014, Sakakura *et al*. (2007) published “Transformation of Carbon Dioxide”, Aresta *et al*. (2013) published “Utilization of CO_2 as a chemical feedstock: opportunities and challenges” and many research on CO_2 utilization, Omae (2012) studying the developments in carbon dioxide utilization for the production of organic chemicals, Nurul Aini Mohamed Razali *et al*. (2012) studying on Heterogeneous catalysts for production of chemicals using CO_2 as raw material. The Direct transformation of carbon dioxide to organic carbonates over heterogeneous catalysts is reported by Dai *et al*., (2009). For chemical recycling of CO_2 to fuels was investigated by Centi & Perathoner (2009). For the methane production, K. Müller *et al*., (2013) and Lars Jürgensen *et al*., (2014) studying on Sabatier based CO_2-methanation of flue gas emitted by conventional power plants and biogas upgrading based on the Sabatier process which using CO_2 as raw material, respectively.

For industrial opportunities for using CO_2 as a chemical feedstock, the aspects discussed in the introduction, it is worthy to briefly summarize some of the opportunities for companies developing R&D activities for conversion of carbon dioxide to fuel and chemicals, or use of CO_2 in chemical processes:

(i) Improvement of the public image for their contribution in converting a CO_2 into valuable chemicals or fuels.

(ii) Development of innovative processes and products.

(iii) Production of liquid fuels from CO_2 which can be able to integrate within the existing infrastructure and having a higher energy density and easier transport/storage than competing solutions (hydrogen, in particular).

(iv) Development of safer chemicals, for example, replacing phosgene with dimethyl carbonate (DMC).

(v) Use of a nontoxic, noncorrosive, and nonflammable reactant, which can be easily stored in liquid form under mild pressure, e.g. safety and environmental benefits in process development

The chemical produced in the greatest amount through CO_2 utilization is urea. According to the international fertilization association, 157 million tons of urea was produced in 2010 (Heffer & Prud'homme, 2010). Other chemicals produced through carbon dioxide utilization are cyclic carbonates, acyclic carbonates, polyalkylene carbonates, Asahi Kasei polycarbonates, carbamic acid esters, oxazolidinones, polyurethanes, carboxylic acids and esters, lactones, formic acid and methanol. The amounts of various organic chemicals produced through carbon dioxide utilization throughout the world are shown in Table 2.1.

Table 2. 1- The production of organic chemicals in the world carbon dioxide utilization (Omae, 2013).

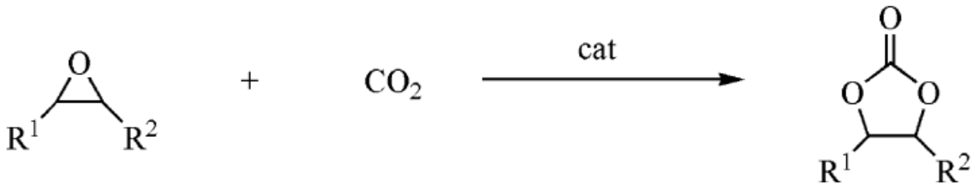
Chemicals	Production (Ton/year)
Cyclic carbonates	80,000
Polypropylene carbonate	76,000
Polycarbonate (Asahi Kasei process)	605,000
Urea	157,000,000

Acetylsalicylic acid	16,000
Salicylic acid	90,000
Methanol	4,000
Inorganic carbonate	30

Highly thermodynamically stable carbon dioxide is now used industrially as a feedstock for the carboxylation of four types of reactive substrates. The first category which is very interesting comprises oxygen-containing compounds, namely epoxides and alcohols. The reactions of reactive epoxides easily proceed at high yields in the presence of various kinds of transition metal compounds, non-transition metal compounds and organic compounds. For the CO_2 utilization the recent developments in carbon dioxide utilization for the production of organic chemicals are review here.

2.1.1 Oxygen-containing compounds

Carbon dioxide reacts with reactive oxygen-containing compounds such as epoxides and alcohols in the presence of a catalyst, as shown in Eqs. (1) and (2).

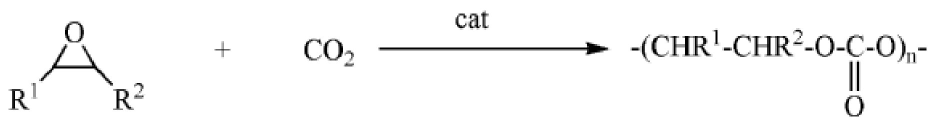


(1)

$$2ROH + CO_2 \xrightarrow{cat} (RO)_2C = O + H_2O \qquad (2)$$

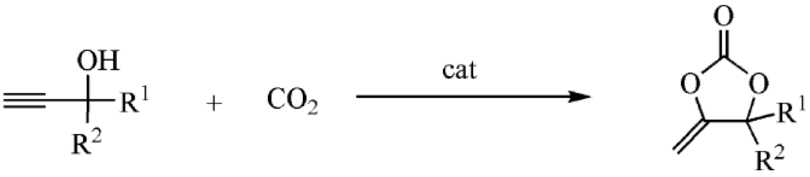
The first reaction (1) proceeds easily with many kinds of catalysts because the epoxides are more reactive compounds than the alcohols. However, the second reaction (2), with alcohols, generally does not proceed in high yield because the reaction yields water and the catalysts are usually deactivated by the water. Hence, these reactions need dehydration agents during the reaction.

The first reaction (1) also proceeds to form polymeric products under reaction conditions described in Section 2.4, as shown in Eq. (3).

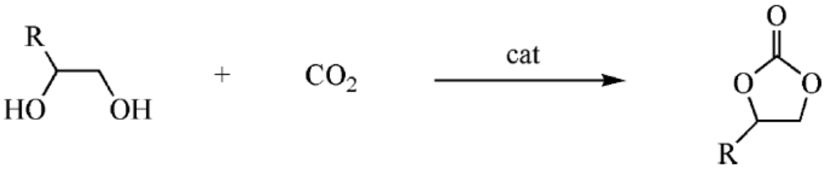


(3)

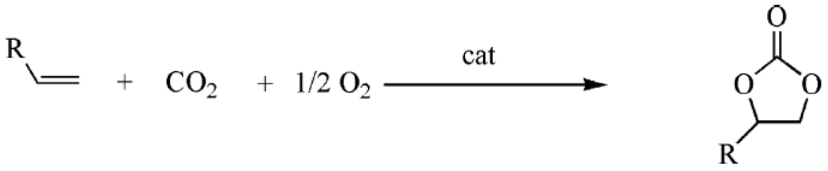
The cyclic carbonates shown in Eq. (1) can also be synthesized through three cyclo carboxylation reactions with reactive substrates such as propargyl alcohols, diols and alkenes, as shown in Eqs. (4)–(6).



(4)



(5)



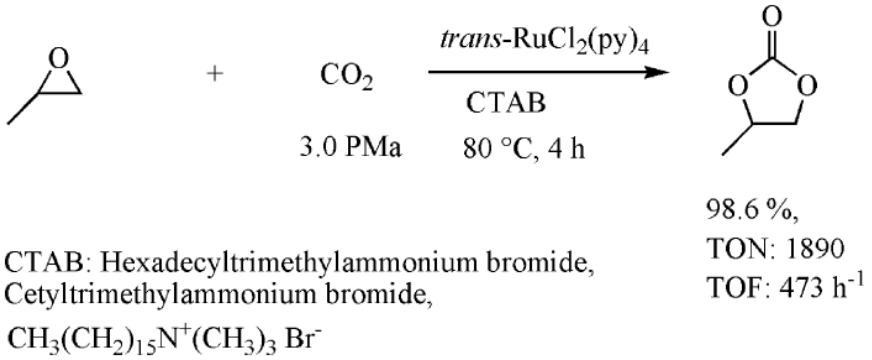
(6)

2.1.2 Cyclic carbonates

Synthesis of cyclic carbonates with epoxides Cyclic carbonates are easily synthesized by the reaction of reactive epoxides with carbon dioxide in the presence of many kinds of catalysts, as shown in Eq. (1). The reported that catalysts such as Cr, Ni, Al, Mg and Sn compounds and ionic liquids induced high yields. Propylene carbonate synthesis in supercritical carbon dioxide ($scCO_2$) with polyfluoroalkyl-phosphonium was an especially effective process because the product spontaneously separated from the $scCO_2$ phase and the catalyst could be recycled while maintaining a high CO_2 pressure and temperature (He et al., 2003). Recently, Ru and Co complexes have been the principle transition metal catalysts, and Ti, Nb, Cr, Re and Au compounds have also been used. The main non-transition metal catalysts used have been Zn and Al compounds as well as Bi and Li compounds. Quaternary ammonium compounds, phosphines, amines and ionic liquids have been used as organic catalysts.

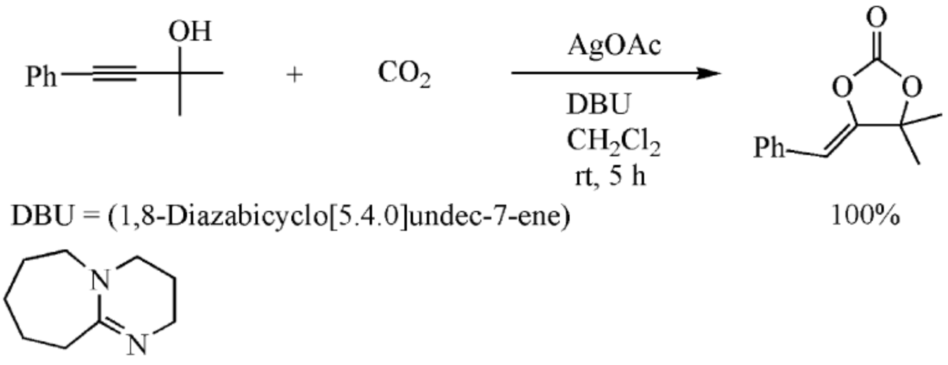
The reaction of propylene oxide with carbon dioxide in the presence of trans-dichlorotetrapyridineruthenium(II) together with CTAB (cetyltrimethylammonium bromide) produces propylene carbonate in a high yield, with a high turnover number

(TON, Moles of product produced per mole of catalyst) and a high turnover frequency (TOF, Moles of product produced per hour), as shown in Eq. (7) (Bu et al., 2010).



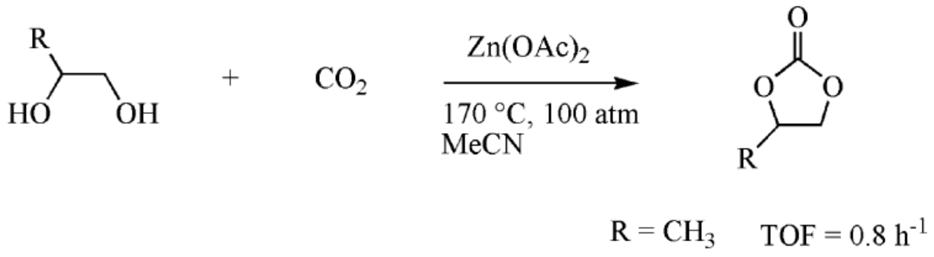
(7)

Cyclocarboxylation with propargyl alcohols. Reactive propargyl alcohols react with carbon dioxide in a reaction similar to the epoxide reactions shown in Eqs. (1) and (7) to give cyclic carbonates, as shown in Eq. (8) (Yamada et al., 2007).



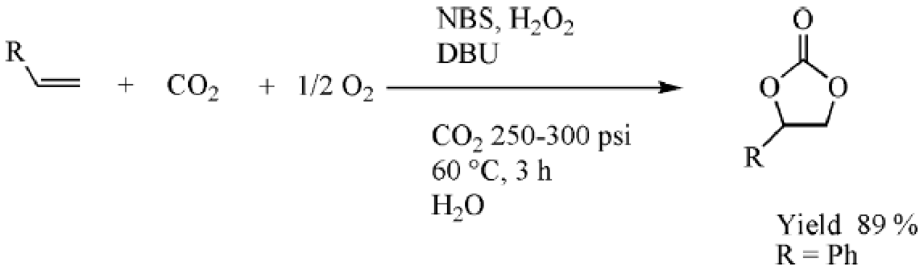
(8)

Cyclocarbonylation with 1,2-diols. Cyclic carbonates are also synthesized by the reaction 1,2-diols such as 1,2-propylene glycol with carbon dioxide in the presence of a catalyst, e.g., anhydrous zinc acetate, in acetonitrile, as shown in Eq. (9) (North et al., 2010).



(9)

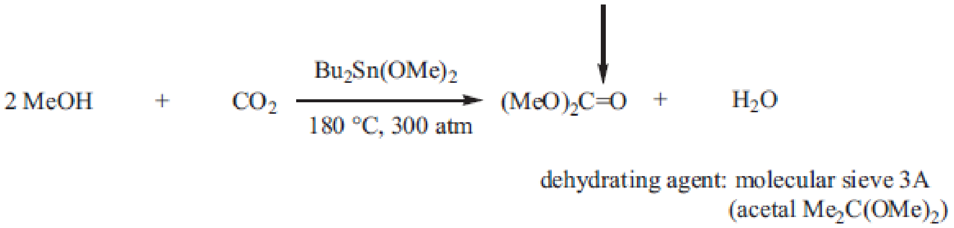
Cyclocarbonylation with alkenes. Alkenes and carbon dioxide are cyclized directly in water with N-bromosuccinimide (NBS) (10% molar) and aqueous hydrogen peroxide with DBU at a high yield, as shown in Eq. (10) (Eghbali and Li, 2007).



(10)

2.1.3 Acyclic carbonates

As shown in Eq. (2), the carboxylation of alcohols yields acyclic carbonates and water. This process usually has a low yield because of the formation of water, especially in the synthesis of dimethyl carbonate. Recently, Sakakura et al. (2009) reported two excellent processes using an acetal and a molecular sieve (3A) as dehydrating agents in the presence of a $Bu_2Sn(OMe)_2$ catalyst as shown in Eq. (11). The process using the acetal gives methyl carbonate in high yield because it is easy to utilize acetone, a byproduct, as the raw material for a reaction with methanol. Therefore, methyl carbonate is synthesized through the reaction of MeOH and CO_2. The other dimethyl carbonate process, using the 3A molecular sieve, involved directly reacting carbon dioxide with methyl alcohol, with dehydration occurring in a separate apparatus at a low temperature (Choi et al., 2002).



(11)

A green, rapid and continuous hydrothermal flow synthesis (CHFS) route has been used to produce highly stable and active novel ceria–zirconia oxide/graphene nanocomposite catalyst [Ce–Zr oxide/graphene, where nominal atomic ratio of Ce:Zr (1:1)]. This catalyst has been investigated by Saada et al., (2015) for the direct synthesis of dimethyl carbonate (DMC) from methanol (MeOH) and carbon dioxide (CO_2) using 1,1,1, trimethoxymethane (TMM) as a dehydrating agent in a high pressure reactor. The resulting grapheme nanocomposites have been further subjected to heat treatment at 973K for four hours in nitrogen. The effect of various reaction conditions, such as reaction temperature, CO_2 pressure, catalyst loading and reaction time has been extensively evaluated. The optimum condition for the direct synthesis of DMC has been found at 383 K, 275 bar and 10% (w/w) catalyst loading. The ceria–zirconia oxide (Ce–Zr oxide)/graphene nanocomposite catalyst showed highest MeOH conversion of 58% at a DMC yield of 33%.

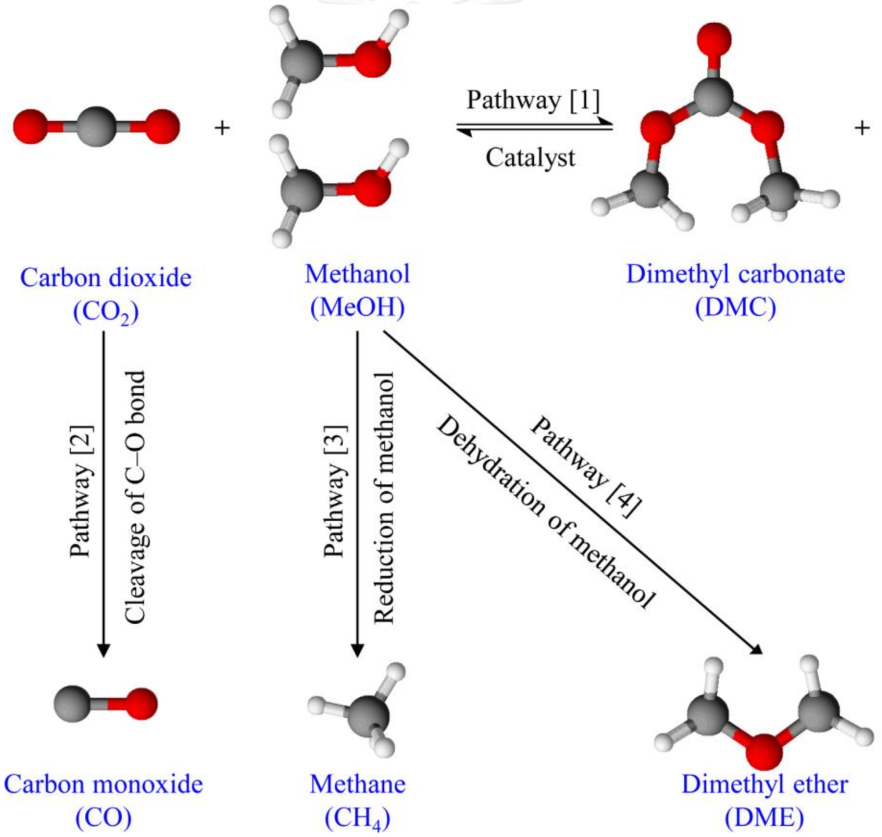


Figure 2.1- Reaction scheme for the synthesis of DMC from MeOH and CO_2.

The second category involves nitrogen containing compounds, where urea is the dominant industrial product which considered already industrialized. Carbon–carbon unsaturated compounds such as aryl compounds, alkynes and alkenes comprise the third category of substrates. The carboxylations of these substrates in the presence of metal compounds such as Cu, Ni and Pd generate the corresponding carboxylic acid derivatives. The five-membered compounds of the cyclometalated substrates can generate the corresponding carboxylic compounds using lithium, rhodium, nickel and palladium compounds as catalysts. The fourth substrate is hydrogen. The expect that the production of formic acid and methanol using hydrogen by utilizing natural energy generation such as geothermal energy and wind power will grow because these products will be in great demand in the near future.

This work is focused on the CO_2 utilization by setting the problem definition "New global target for CO_2 utilization to DMC synthesis" as the objective function. The reduction of the total emission is to design and optimize the sustainable process employing the combined CO_2 utilization section, intermediates production section and final product section. The analysis focuses mainly on thermochemical routes which utilize CO_2 rather than sending these to the atmosphere, it is possible to collect them and use them for other purposes. Targeting some of the largest contributors: power generation, manufacturing, chemical industry, it is possible to determine the amounts available and utilized through process network optimization, to indicate the reduction level of CO_2 and to promote CO_2 as feedstock for producing higher value-added chemicals.

The review technology for DMC production from CO_2 based process are represented in chapter 5, the evaluations of different CO_2-based processes for dimethyl carbonate production are present to indicate the feasibility of CO_2 utilization process and promote the CO_2 conversion by thermochemical routes. The various reaction pathways are represented the preliminary evaluation of conventional process (BAYER process) and CO_2 utilization process (urea route, EC route, PC route). In chapter 6, the integration of methods and tools for design of sustainable CO_2 utilization network for dimethyl carbonate production are present to propose the optimal processing route which respect to objective function. The process analysis, process intensification and process evaluation (economic and life cycle assessment) are included in this chapter.

2.2 Process synthesis-design

Since the term “synthesis” proposed by Rudd, Powers, and Siirola (1973), over the past several decades, process synthesis has had a significant impact on the development, design and operation of (petro) chemical processes. Process synthesis can be considered as the cornerstone of the process design activity. It provides a systematic way to identify the types of equipment, flowrates, operating/design conditions and optimal interconnections among different units that create the best total flowsheet. Traditionally, the synthesis problem can be described as follows: given a set of feedstocks and a set of desired final products with specifications, it is desirable to develop a systematic methodology with various objectives such as the highest yield, the highest energy efficiency or the most sustainable route for the generation of optimal configurations for transforming the raw materials to desired products.

The work from Jaksland & Gani, (1996) has proposed the combined methodology employing appropriate physico-chemical properties' estimation methods, the process synthesis algorithm. In each case, a common set of properties and variables that promote the integration, are identified. The methodology of properties is classified with respect to process synthesis, product/process design and control; identified relationships between properties, process synthesis, process/product design and control are exploited. a framework for computer-aided chemical product design is presented together with a review of methods and tools that may be useful in chemical product design. Gani (2004) proposed the framework is to provide a set of integrated methods and tools so that some of the chemical product designs steps can be carried out faster, over a wider search space and using less resources. The requirements for such a framework and its resident methods and tools are that there exists a reliable set of models. Within this context, the differences between the process model, the property model and the chemical product model are highlighted together with a discussion on the roles of property models with respect to chemical product design.

Considering the concept of a biorefinery, a facility that integrates biomass conversion processes and equipment to produce chemicals, fuels and power - the four chemical products can be identified from multiple products that are commonly attributed to a biorefinery have been proposed by Alvarado-Morales et al., (2008). The first step is to evaluate a base case design and define targets for generation of more sustainable alternatives. In this way, an analogy may be drawn with computer aided molecular design (CAMD), where molecules matching a set of target properties are identified. Bommareddy et al., (2011) proposed a systematic group contribution based framework is for synthesis of process flowsheets from a given set of input and output specifications. Analogous to the group contribution methods developed for molecular design, the framework employs process groups to represent different unit operations in the system. Feasible flowsheet configurations are generated using efficient combinatorial algorithms and the performance of each candidate flowsheet is evaluated using a set of flowsheet properties.

The systematic way in the biorefinery processes for converting biomass derived carbohydrates into transportation fuels and chemicals has been proposed by Yuan et al., (2013). Process synthesis, which has played a vital role for the development, design and operation of (petro) chemical processes, can be predicted to play a significant role in the design and commercialization of sustainable and cost-effective biorefinery processes.

The process synthesis-design in minimizing raw material and energy usage without compromising on economics was proposed by Halim et al., (2011). The computer tools are available to assist in sustainability assessment, their applications are constrained to a specific domain of the design synthesis problem. Their work outlines a design synthesis strategy that integrates two computer methodologies ENVOPExpert and SustainPro for simultaneous generation, analysis, evaluation, and optimization of sustainable process alternatives.

The study used process synthesis and design for solving the complexity of this network such as GAMS for using as optimization tool and SustainPro for finding the hotspot in the process (Carvalho *et al*., 2008 & Quaglia *et al*., 2012, 2013). The selected processes and the feasible networks are generated and simulated to verify the initial synthesis design results. Integrated process synthesis and design are generated and collected as the data input for superstructure. The process intensification method “phenomena based synthesis” was included for solving the process hot-spots. The performance indicators used are such as net CO_2 emission from the process, CO_2 reduction from feedstock usage combined with the sustainability metrics, economic analysis with ECON(Saengwirun, 2011) and life cycle assessment which using LCSoft (Kalakul *et al*., 2014). All of performance indicators are used to identify the final process, amount of CO_2 reduction and utilization and to achieve more sustainable design.

2.3 Sustainability and process design

2.3.1 Process analysis

A knowledge-based simulation-optimization framework and system for sustainable process operations has been proposed by Halim & Srinivasan (2011), the Design and operation of chemical plants involves a combination of synthesis, analysis and evaluation of alternatives. Such activities have traditionally been driven by economic factors first, followed by engineering, safety and environmental considerations. Recently, chemical companies have embraced the concept of sustainable development, entailing renewable feed materials and energy, non-toxic and biodegradable products, and waste minimization or even elimination at source. The proposed of a knowledge based simulation-optimization framework for generating sustainable alternatives to chemical processes. The framework has been developed by combining different process systems engineering methodologies-the knowledge-based approach for identifying the root cause of waste generation, the hierarchical design method for generating alternative designs, sustainability metrics, and multi-objective optimization into one coherent simulation-optimization framework. This is implemented as a decision-support system and the HYSYS process simulator. The illustrated of the framework and system using the HDA and biodiesel production case studies is represented in Figure 2.2.

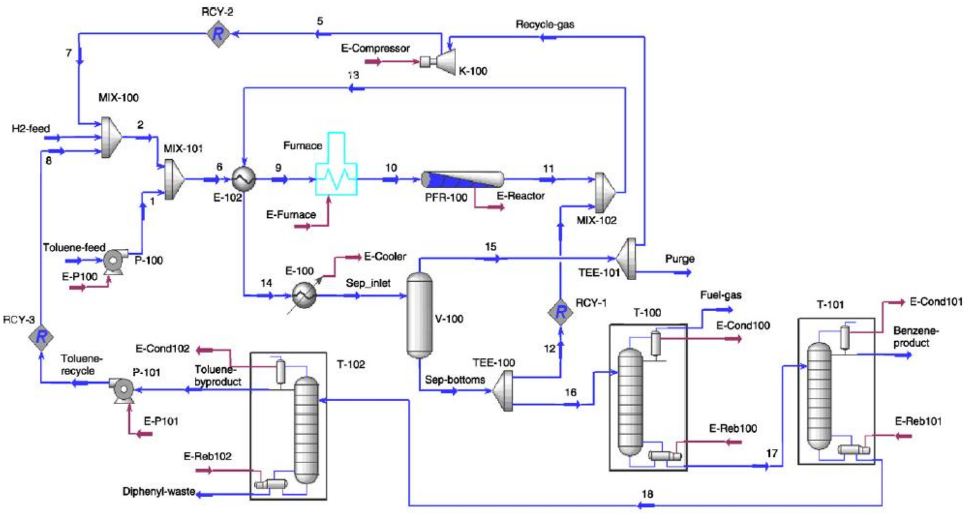


Figure 2.2 - Flowsheet of hydro-dealkylation process.

In this HDA process, the useless materials (impurities) that enter with the feed in the inlet stream will inevitably lead to waste. Useful material in the inlet stream may become waste when they are in excess or transformed at low conversion rates and not adequately recovered. The term ineffective separation is used to describe a separation that causes an escape of non-waste materials (i.e. raw materials, products or solvents) into a waste stream (Halim & Srinivasan, 2002). Waste generating operations are identified based on information of the status of the material. The presence of a product material in the waste stream, for example, is detrimental. Likewise, a waste material present in the product stream. An ineffective separation can be flagged if there is a material that is detrimental in the waste stream, yet desirable in other streams. The next step is to find the intersecting separation operation which leads to the escape of such material into the former stream.

In the example in Figure 2.3, we can identify that the stabilizer and benzene columns lead to the escape of desirable methane and benzene into the waste streams. Therefore, they are the ineffective separators. Such analysis, when performed on all components in the waste streams, reveals the following waste sources in the HDA process:

1. Excessive raw materials in the H_2 and toluene streams leading to their presence in the purge and waste streams,

2. Diphenyl byproduct and low conversion of toluene and hydrogen in the reactor,

3. Inefficient methane separation in stabilizer column (T-100),
4. Inefficient benzene separation in benzene column (T-101), and
5. Inefficient toluene separation in toluene column (T-102).

The subsequent step after diagnosing the waste sources is to derive decision solutions to eliminate them.

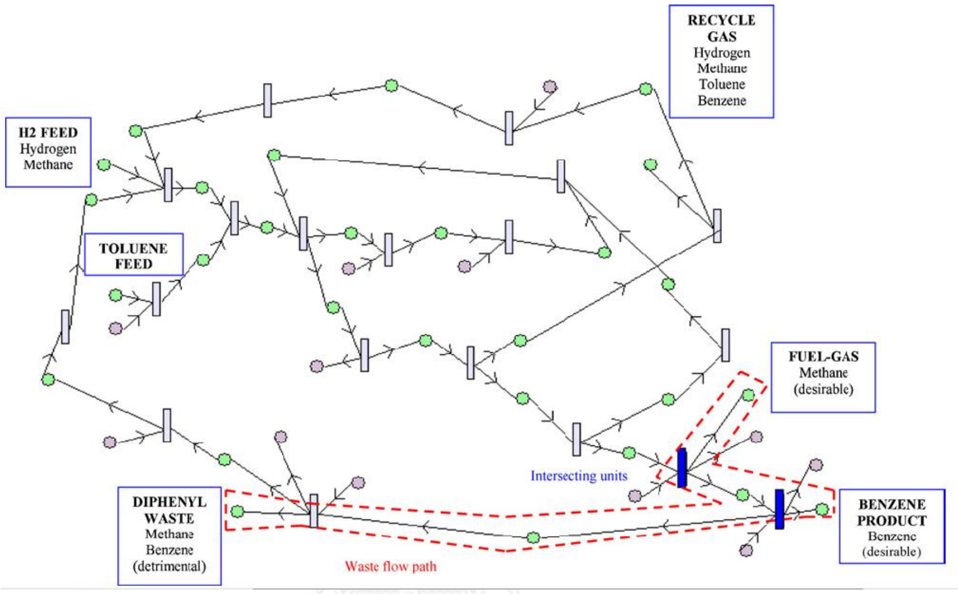


Figure 2.3 - P-graph model of HDA process for process analysis.

In addition, a generic and systematic methodology for identifying the feasible retrofit design alternatives of any chemical process has proposed by Carvalho *et al.*, (2008) and the extended systematic methodology using process information/data such as the process flowsheet, the associated mass/energy balance data and the cost data, SustainPro guides the user through the necessary steps according to work-flow of the implemented methodology (Carvalho et al., 2013). The methodology determines a set of mass and energy indicators from steady-state process data, establishes the operational and design targets, and through a sensitivity-based analysis, identifies the design alternatives that can match a set of design targets. The significance of this indicator based method is that it is able to identify alternatives, where one or more performance criteria (factors) move in the same direction thereby eliminating the need to identify trade-off based solutions. These indicators are also able to reduce (where feasible) a set of safety indicators. An indicator sensitivity analysis algorithm has been added to the methodology to define design targets and to generate sustainable process alternatives. A computer aided tool has been developed to facilitate the calculations needed for the application of the methodology. The application of the indicator-based methodology and the developed software are highlighted through a process flowsheet for the production of vinyl chlorine monomer (VCM).

The systematic framework was represented in Figure 2.4 in six step of indicator-based methodology as presented in previous chapter. The used of sustainability metric as performance indicators for process evaluation was shown in Figure 2.5.

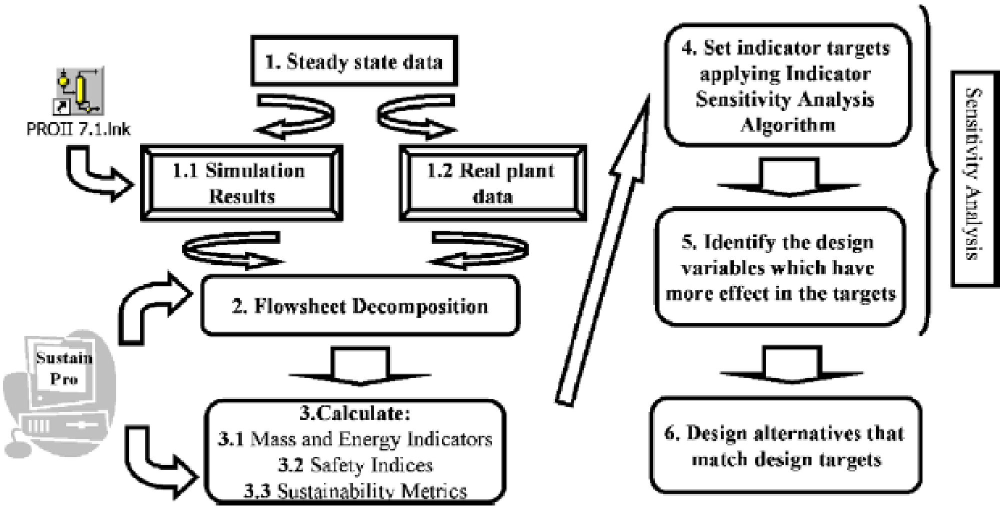


Figure 2.4 – Flow diagram of the indicator-based methodology. (Carvalho *et al*., 2008).

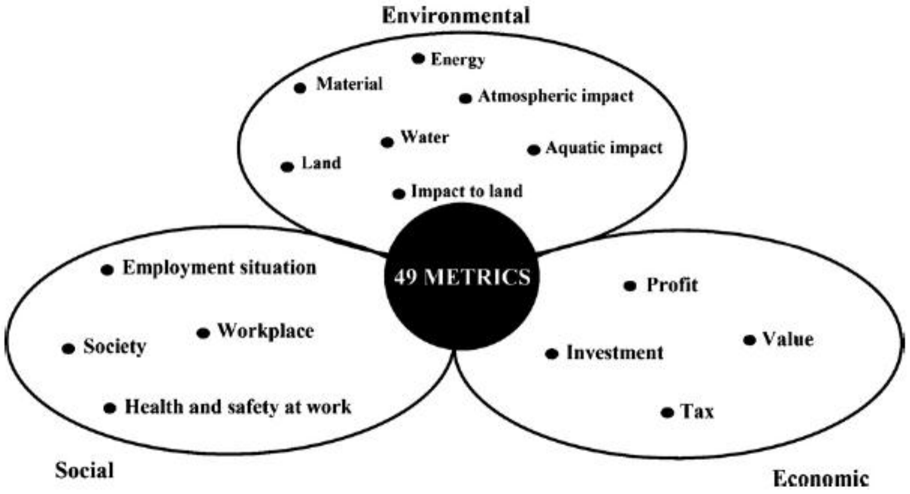


Figure 2.5 – Example of the sustainability metrics proposed by Azapagic (2002).

The VCM case study, indicated the open-path and closed-path as shown in Figure 2.6 and from SustainPro analysis, it could identify the most relevant paths which considered as “hot-spots” as represented in Table 2.2 and the result given in Table 2.3.

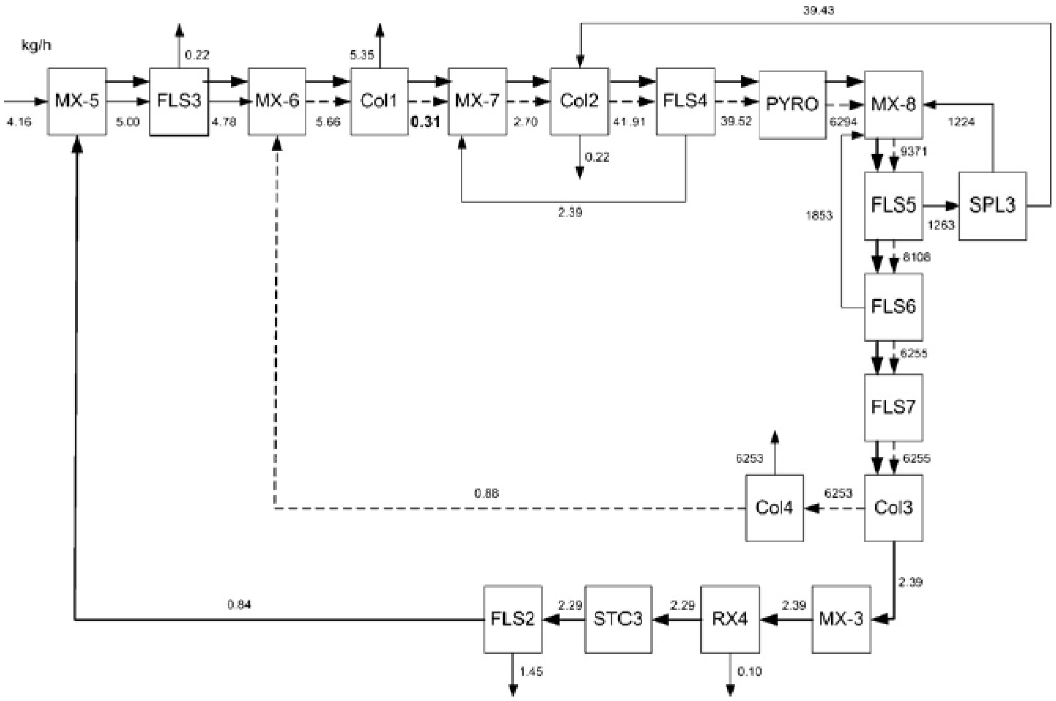
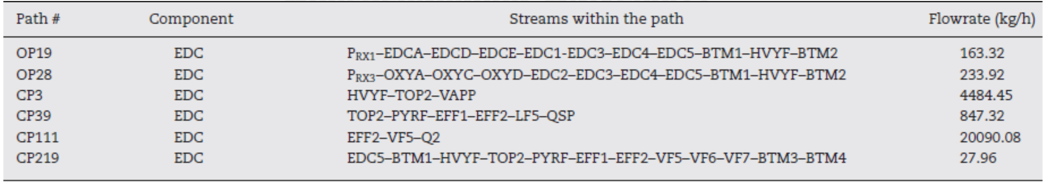


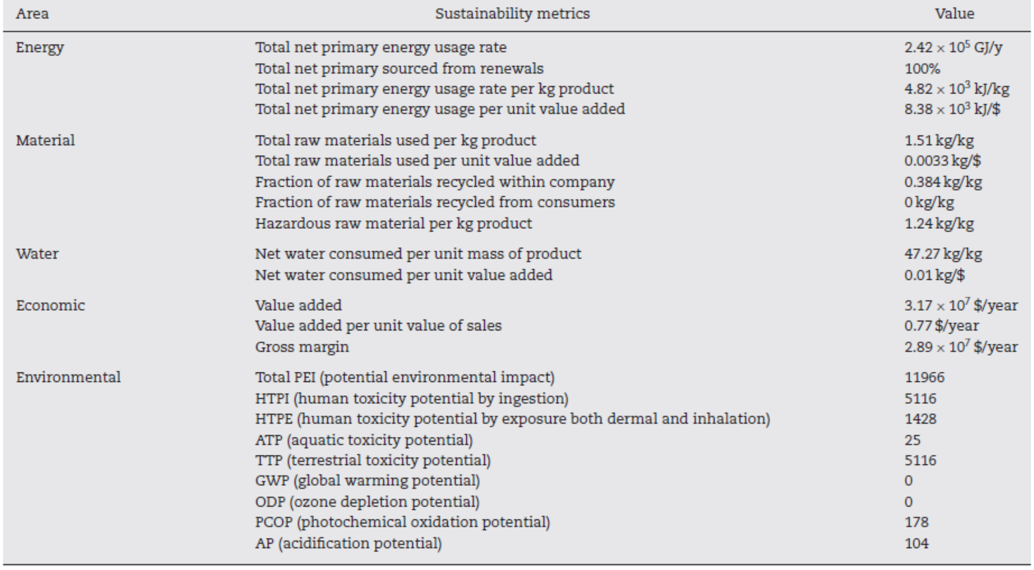
Figure 2.6 – Flowrates of VCM in the nested loops of VCM process flowsheet.

Table 2.2 – Identification of the most relevant paths – VCM case study. (modified from Carvalho *et al*., 2008)



Path #	Component	Streams within the path	Flowrate (kg/h)
OP19	EDC	P_{RX1}–EDCA–EDCD–EDCE–EDC1-EDC3–EDC4–EDC5–BTM1–HVYF–BTM2	163.32
OP28	EDC	P_{RX3}–OXYA–OXYC–OXYD–EDC2–EDC3–EDC4–EDC5–BTM1–HVYF–BTM2	233.92
CP3	EDC	HVYF–TOP2–VAPP	4484.45
CP39	EDC	TOP2–PYRF–EFF1–EFF2–LF5–QSP	847.32
CP111	EDC	EFF2–VF5–Q2	20090.08
CP219	EDC	EDC5–BTM1–HVYF–TOP2–PYRF–EFF1–EFF2–VF5–VF6–VF7–BTM3–BTM4	27.96

Table 2.3 – Calculated sustainability metrics – VCM case study. (modified from Carvalho *et al*., 2008).



Area	Sustainability metrics	Value
Energy	Total net primary energy usage rate	2.42×10^5 GJ/y
	Total net primary sourced from renewals	100%
	Total net primary energy usage rate per kg product	4.82×10^3 kJ/kg
	Total net primary energy usage per unit value added	8.38×10^3 kJ/$
Material	Total raw materials used per kg product	1.51 kg/kg
	Total raw materials used per unit value added	0.0033 kg/$
	Fraction of raw materials recycled within company	0.384 kg/kg
	Fraction of raw materials recycled from consumers	0 kg/kg
	Hazardous raw material per kg product	1.24 kg/kg
Water	Net water consumed per unit mass of product	47.27 kg/kg
	Net water consumed per unit value added	0.01 kg/$
Economic	Value added	3.17×10^7 $/year
	Value added per unit value of sales	0.77 $/year
	Gross margin	2.89×10^7 $/year
Environmental	Total PEI (potential environmental impact)	11966
	HTPI (human toxicity potential by ingestion)	5116
	HTPE (human toxicity potential by exposure both dermal and inhalation)	1428
	ATP (aquatic toxicity potential)	25
	TTP (terrestrial toxicity potential)	5116
	GWP (global warming potential)	0
	ODP (ozone depletion potential)	0
	PCOP (photochemical oxidation potential)	178
	AP (acidification potential)	104

Morales *et al*., (2009) have present the all refineries are characterized by mixed feedstocks and a range of products as shown in Figure 2.7, but biorefineries in particular can involve a very diverse range of 'bio' related material (of variable quality) as a feedstock. The subsequent processing steps may involve heterogeneous catalysis, immobilized enzymes, homogeneous catalysts, soluble enzymes, fermentations or combinations thereof, alongside purification steps. This presents a particularly interesting process integration challenge since the optimal conditions for each process step will be considerably different to each other, there are large temperature gradients through the process and a significant amount of water is used. The basic question to address is thus which product to produce and which sequence of unit operations to apply to obtain the highest profit for the biorefinery. Use of a systematic methodology to analyze and improve processing routes for a specific biorefinery product is therefore a useful first step in the evaluation of the biorefinery product tree. The use of a systematic methodology for design and analysis are using in bioethanol production as an example. More specifically, consider a well-known bioethanol production route, analyze it with respect to cost, operation and sustainability, and based on these, generate new alternatives with respect to waste reduction (water) and efficient downstream separation.

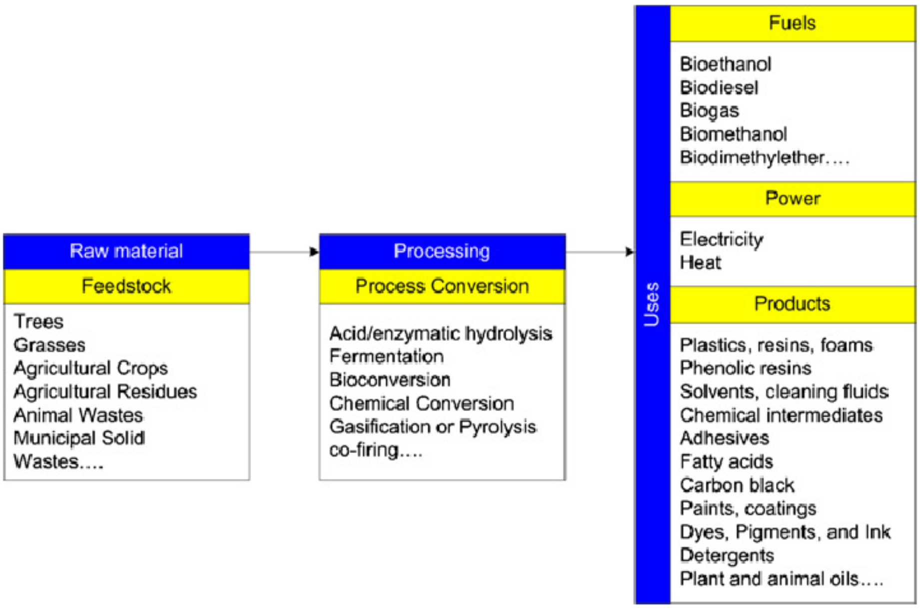


Figure 2.7 – Biorefinery products from renewable feedstocks. (modified from Morales *et al*., 2009).

Case study: bioethanol production process

The base case of a bioethanol production process considered here is the NREL process (Wooley *et al*., 1999). In this case study, the specification is considering the production of 52.7 Mgal/year of 99.95% pure ethanol from lignocellulosic biomass, where the hydrolytic enzyme is purchased.

- Base case design

A base case (Wooley *et al*., 1999) of the bioethanol production process is based on the one given by NREL. The main operations of the process are highlighted in Figure 2.8.

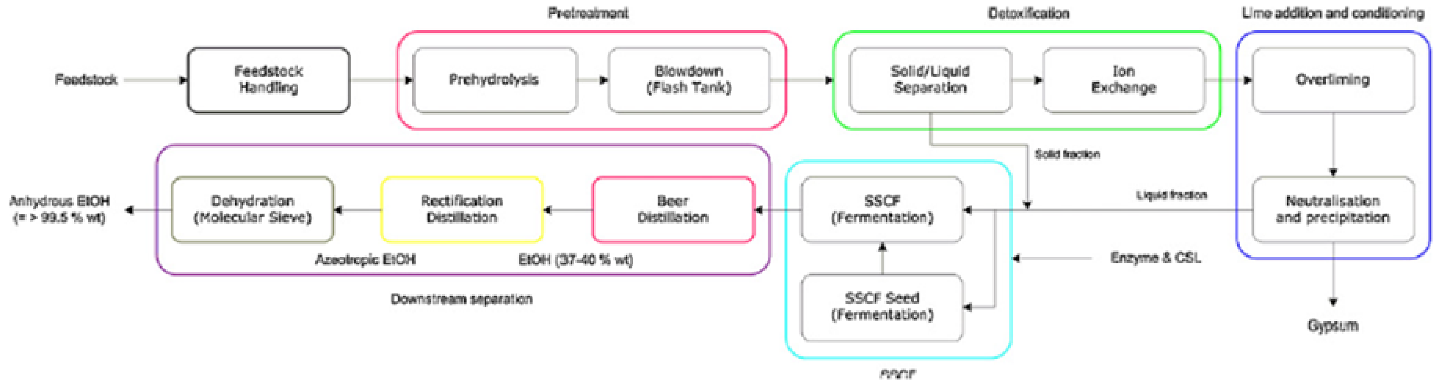


Figure 2.8 – Base case: bioethanol production process flowsheet from lignocellulosic biomass based on the NREL process (Wooley et., 1999). (CSL = corn steep liquor)

Feedstock handling: The feedstock, in this case hardwood chips, is delivered to the feed handling area for storage and size reduction. Pre-treatment: The heart of the pre-treatment process area is the “pre-treatment reactor”, which converts most of the hemicellulose portion of the feedstock to soluble sugars – primarily xylose, mannose, arabinose and galactose by hydrolysis using dilute sulfuric acid and elevated temperature.

The hydrolysis under these conditions also solubilizes some of the lignin in the feedstock. In addition, acetic acid is released from the hemicellulose hydrolysis. Degradation products of pentose sugars (primarily furfural) and hexose sugars (primarily hydroxymethylfurfural) are also formed. Following the pre-treatment reactor, the hydrolysate consisting of a mixture of liquid and solid particles is flash cooled. This operation vaporizes a large amount of water, a portion of acetic acid, and much of the furfural and hydroxymethylfurfural. Removing these heterocyclic aldehydes is beneficial, as they can be toxic to the microorganisms in the downstream fermentation (Wooley *et al*., 1999). Detoxification, lime addition and conditioning: In addition to flash removal of the aldehydes, the unreacted solid phase is separated from the liquid hydrolysate. The latter contains sulfuric acid and other inhibitors in addition to the hemicellulose sugars.

Before fermentation, detoxification of the liquid hydrolysate is required to remove the inhibitors formed during the pre-treatment of biomass. Ion exchange is used to remove acetic acid and sulfuric acid that will be toxic to the microorganisms in the fermentation. After ion exchange the pH is raised to 10 (by adding lime) and held at this value for a period of time. Neutralisation and precipitation of gypsum follow the overliming step. The gypsum is removed via filtration and the hydrolysate is finally mixed again with the solid fraction (from the solid–liquid detoxification separation unit) before being sent to SSCF. SSCF: Following the lime addition, a small portion of the detoxified slurry is diverted to the simultaneous saccharification and co-fermentation (SSCF) seed process area for microorganism production (Zymomonas mobilis) while the bulk of the material is sent to the (SSCF) process area. Two different operations are performed in this process area saccharification (hydrolysis) of the remaining cellulose to glucose using cellulase, and fermentation of the resulting glucose and other sugars to ethanol. The enzyme used in the saccharification is assumed to be purchased from an enzyme manufacturer. For the fermentation, the recombinant Z. mobilis bacterium is used, which will ferment both glucose and xylose to ethanol. A seed inoculum, nutrients, enzyme, and the detoxified slurry are added to a train of continuous fermenters.

The resulting ethanol broth is collected and sent to the downstream separation area. Downstream separation: After the SSCF, distillation and molecular sieve adsorption are used to recover the ethanol from the fermenter beer and produce nearly 100% pure ethanol. Distillation is accomplished in two columns. The first column (beer column) removes the dissolved CO_2 and most of the water, and the second distillation column concentrates the ethanol to near azeotropic composition. Subsequently, the residual water from the nearly azeotropic mixture is removed by vapor phase molecular sieve adsorption.

- Generate data for analysis

The overall flowsheet was simulated using the PROII (PROII, 2006) simulator. Parts of the physical property data for simulation were obtained from Wooley *et al*. (1999) and others were estimated using the method of Marrero *et al*., (2001) for pure component property estimation. The feedstock composition and operating conditions were taken from Wooley *et al*., (1999) and Hamelinck *et al*., (2005). Each part of the process (feedstock handling, pre-treatment, detoxification, lime addition, fermentation (SSCF), and ethanol recovery/purification) has been analyzed in detail together with a breakdown of the operating and capital costs of the different parts of the bioethanol production process. Once the operational and equipment costs were determined, the manufacturing cost of the bioethanol production process was calculated.

- Define targets for design alternatives

First, process economy and process points where the basecase design can be improved were analyzed. Then, targets for improvement have been defined.

  - Economic analysis

A plant producing, 52.7 Mgal/year of ethanol and operating 8406 h per year has been used as a base case. The feedstock rate is taken to be 159,116 kg/h. The total annual manufacturing cost was found to be 1.92 USD/gal ethanol and includes the costs for the process equipment, for steam and cooling water and other miscellaneous costs. The miscellaneous costs include feedstock, electricity, process water, general and administrative expenses, employee salaries, chemicals, enzyme and maintenance. The physical sizing of equipment units as well as the cost estimation for most of the equipment was done following the method given by Biegler *et al.*, (1999). The results are summarized in Table 2.4, and Figure 2.9 shows the breakdown of the manufacturing cost.

Table 2.4 – Main characteristics of the base case.

Ethanol production rate	52.7	Mgal/year
Purity	99.95	Wt.%
Operating hours per year	8406	h/year
Enzyme cost	1.5	USD/kg
Total equipment cost	49.05	MUSD
Total manufacturing cost	101.39	MUSD/year
Total manufacturing cost	1.92	USD/gal

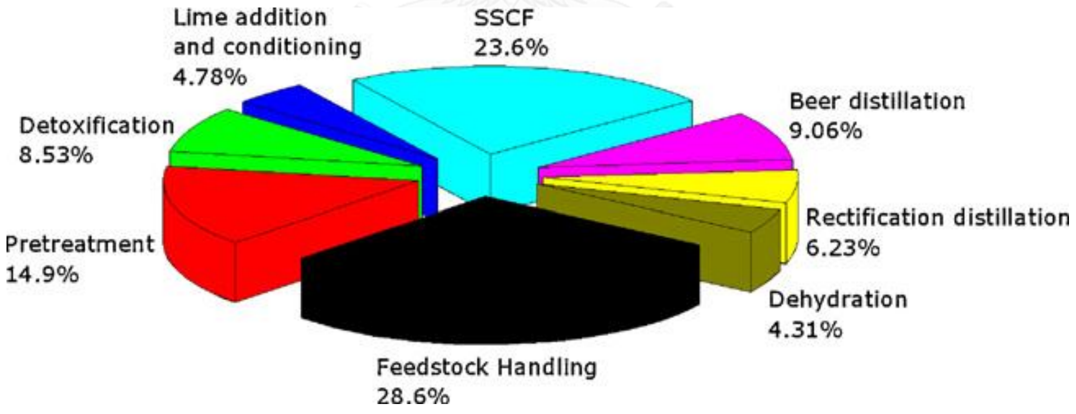


Figure 2.9 – Breakdown of the total bioethanol manufacturing cost according to the different parts of the process flowsheet.

The process flowsheet and the corresponding stream summary obtained through simulation with PROII$^{®}$ are given in Figure 2.10.

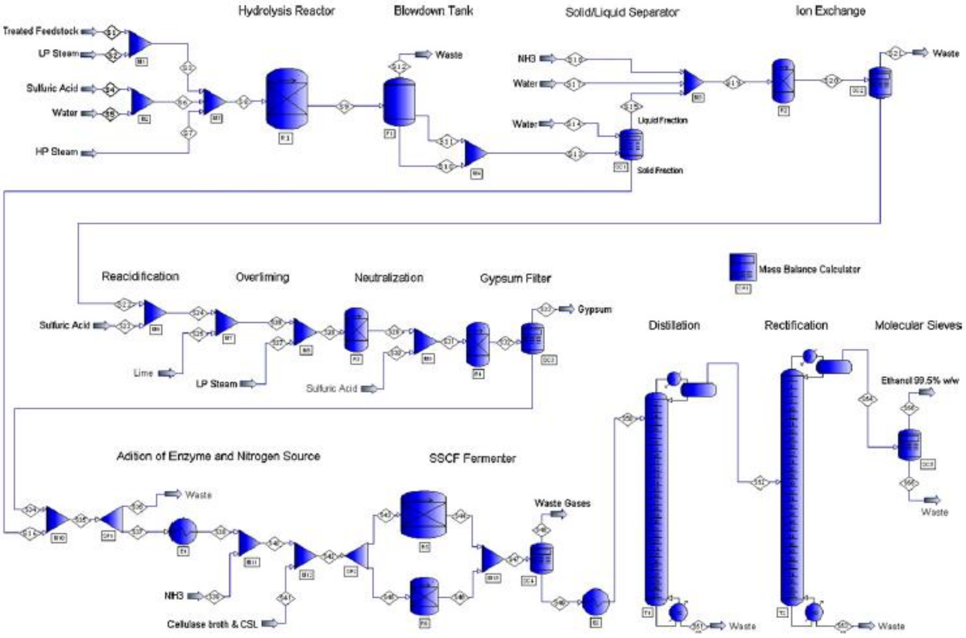
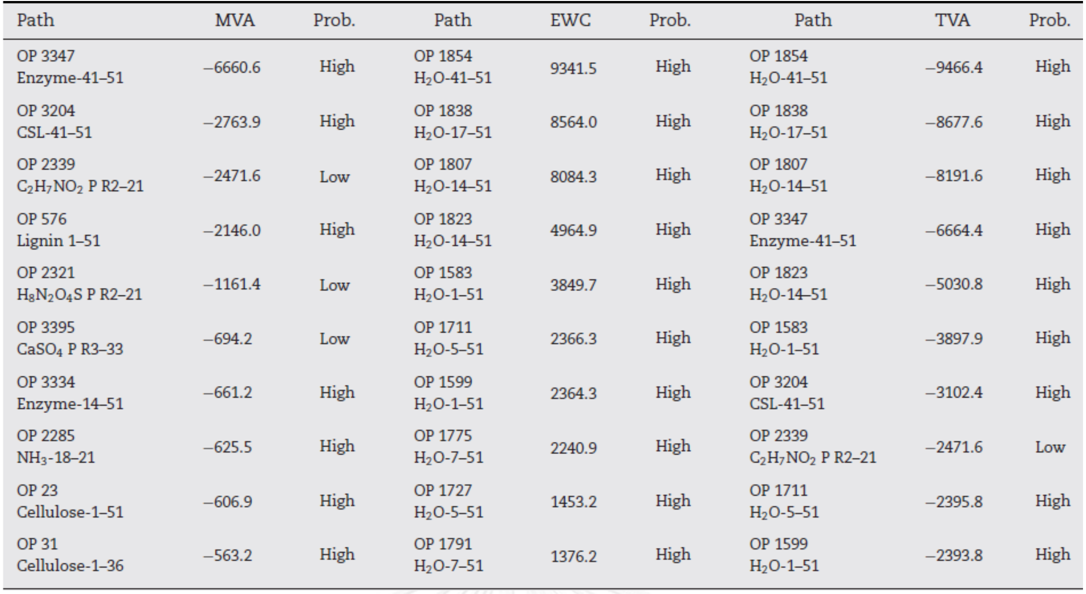


Figure 2.10 - The process flowsheet of bio-ethanol production process.

- Indicator-based analysis of process flowsheet

The SustainPro software has been applied to the base case. For the process flowsheet (see Appendix A) and the results of the mass and energy balances, SustainPro calculated 3437 open-path (OP) indicators. Since the process flowsheet does not have any recycle streams, there are no closed-path (CP) indicators. Table 2.5 lists the indicators for the OPs with the highest (absolute) indicator values.

Table 2.5 – List of the most sensitive indicators for the open-paths (OP’s). (modified from Morales *et al*., 2009).



Path	MVA	Prob.	Path	EWC	Prob.	Path	TVA	Prob.
OP 3347 Enzyme-41–51	−6660.6	High	OP 1854 H_2O-41–51	9341.5	High	OP 1854 H_2O-41–51	−9466.4	High
OP 3204 CSL-41–51	−2763.9	High	OP 1838 H_2O-17–51	8564.0	High	OP 1838 H_2O-17–51	−8677.6	High
OP 2339 $C_2H_7NO_2$ P R2–21	−2471.6	Low	OP 1807 H_2O-14–51	8084.3	High	OP 1807 H_2O-14–51	−8191.6	High
OP 576 Lignin 1–51	−2146.0	High	OP 1823 H_2O-14–51	4964.9	High	OP 3347 Enzyme-41–51	−6664.4	High
OP 2321 $H_8N_2O_4S$ P R2–21	−1161.4	Low	OP 1583 H_2O-1–51	3849.7	High	OP 1823 H_2O-14–51	−5030.8	High
OP 3395 $CaSO_4$ P R3–33	−694.2	Low	OP 1711 H_2O-5–51	2366.3	High	OP 1583 H_2O-1–51	−3897.9	High
OP 3334 Enzyme-14–51	−661.2	High	OP 1599 H_2O-1–51	2364.3	High	OP 3204 CSL-41–51	−3102.4	High
OP 2285 NH_3-18–21	−625.5	High	OP 1775 H_2O-7–51	2240.9	High	OP 2339 $C_2H_7NO_2$ P R2–21	−2471.6	Low
OP 23 Cellulose-1–51	−606.9	High	OP 1727 H_2O-5–51	1453.2	High	OP 1711 H_2O-5–51	−2395.8	High
OP 31 Cellulose-1–36	−563.2	High	OP 1791 H_2O-7–51	1376.2	High	OP 1599 H_2O-1–51	−2393.8	High

- Define targets

Analyzing the indicators from Table 2.5, it can be concluded that there is a large waste of the raw material and utilities. For example, the MVA (material value added) indicator corresponding to OP 576 indicates that the raw material in the form of lignin is being wasted (because the MVA has a large negative value). For OP 1807, the EWC (energy and water cost) is 8084 while the TVA (total value added) is -8192. This indicates that water in this stream uses a lot of energy (positive EWC) and is losing its value (negative TVA) as it enters and leaves the process. The sensitivity analysis step of SustainPro then determines that the OP 1807 has the highest potential to result in an improvement in terms of TVA (water use) and EWC (energy cost due to use of water).

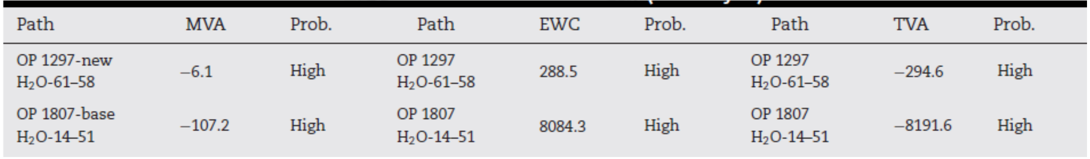
- Generate design alternatives

Two options have been considered. Reduction of water (in order to reduce the open-path MVA values) and alternatives for downstream separation (in order to improve process energy and operating costs, without increasing the environmental impact).

- Removal of water

The first attempt to generate alternatives was to identify possibilities of reducing the TVA in OP 1807 (see Table 2.5) by reducing the amount of water leaving the system (that is, minimizing the fresh water requirement with respect to OP 1807). An obvious solution for reduction of fresh water is by treating the water and recycling it after the beer distillation. After adding this recycle and water recovery step, and recalculating the indicators, SustainPro confirms that the TVA for water has indeed been improved, thereby improving the sustainability metrics related to waste. Table 2.6 lists the new values of the OPs for the MVA, TVA and EWC indicators. Note that because the amount of water needed for pre-treatment, detoxification and SSCF operations have not been reduced, the EWC has also not been reduced. This indicates that process improvement with respect to reduction of water will not reduce the energy consumption of the process. Therefore, the subsequent life cycle assessment which is primarily based on energy usage, does not show significant improvement.

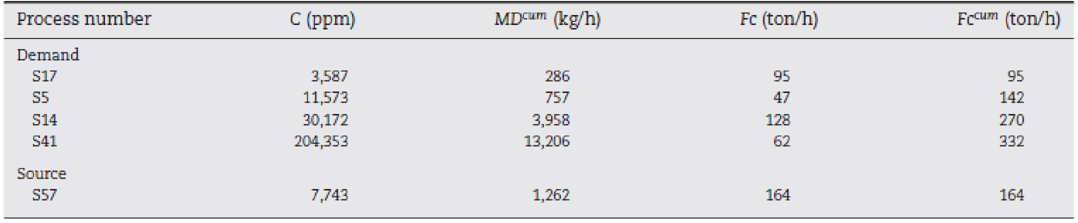
Table 2.6 – New values of the indicators for the new flowsheet alternative (with recycle). (modified from Morales *et al*., 2009).



Path	MVA	Prob.	Path	EWC	Prob.	Path	TVA	Prob.
OP 1297-new H_2O-61–58	−6.1	High	OP 1297 H_2O-61–58	288.5	High	OP 1297 H_2O-61–58	−294.6	High
OP 1807-base H_2O-14–51	−107.2	High	OP 1807 H_2O-14–51	8084.3	High	OP 1807 H_2O-14–51	−8191.6	High

The above alternative could also have been obtained through a water-pinch analysis (Liu *et al*., 2007) using the extracted data of the involved streams (see Table 2.7). The objective is to reduce the amount of fresh water to be added to the system by reusing the water from other streams. Table 2.7 shows the process data for demand and source streams for the bioethanol process base case. Multiple impurities are almost always present in this type of process. With the purpose of analyzing the reuse of wastewater, impurities can sometimes be lumped in a single pseudo-impurity or ignored if their concentration is low. In this case all the impurities present in the streams were lumped in a single pseudo-impurity whose concentration is represented by C (ppm) in the second column of Table 2.7.

Table 2.7 – The process data for the bioethanol process (base case design). (modified from Morales *et al*., 2009).



Process number	C (ppm)	MD^{cum} (kg/h)	Fc (ton/h)	Fc^{cum} (ton/h)
Demand				
S17	3,587	286	95	95
S5	11,573	757	47	142
S14	30,172	3,958	128	270
S41	204,353	13,206	62	332
Source				
S57	7,743	1,262	164	164

In Figure 2.11 the last column in Table 2.7 (x-axis) is plotted against the third column (y-axis). Accordingly the plot of cumulative flowrate against cumulative mass load (for demand and supply streams) indicated a pinch at 164 ton/h (water recycled). This point satisfies the condition given by Liu *et al*. (2007) for the minimum amount of fresh water needed (12.1 ton/h).

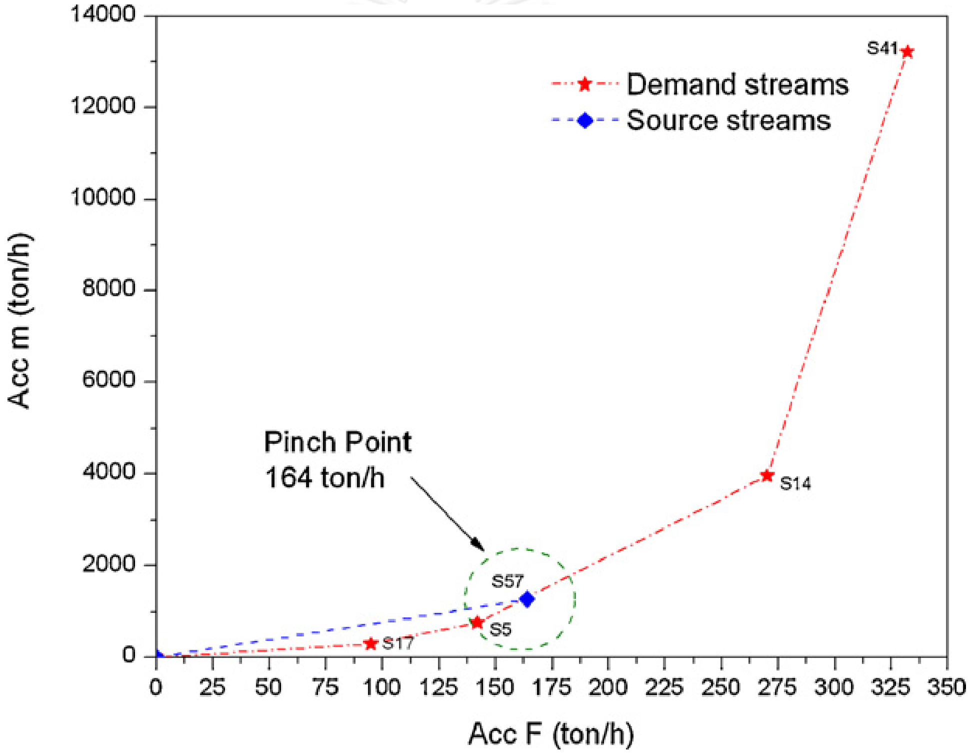


Figure 2.11 – Water composite curves for the process base case. (modified from Morales *et al*., 2009).

- Downstream separation

The product stream from the fermentation stage in the bioethanol production process from lignocellulosic biomass is a mixture of ethanol, cell mass and water. Interestingly, in this stream, the ethanol concentration from lignocellulosic biomass is lower than that from corn. To obtain anhydrous ethanol, the first step is to recover ethanol from the product stream of the fermenter. The product from the beer distillation (37 wt.% ethanol) is then concentrated to obtain anhydrous ethanol (more than or equal to 99.5 wt.%). The downstream separation is therefore defined as the separation task related to obtaining anhydrous ethanol from an ethanol–water mixture. Two options to be considered (and evaluated) are the use of organic solvents and ionic liquids.

Organic solvent: Since the ethanol–water mixture forms a homogeneous minimum-boiling azeotrope of 95.6 wt.% ethanol at 78.15 °C and 101.3 kPa, one way to separate the mixture into two pure products is to use a solvent-based separation, such as extractive distillation (Huang *et al*., 2008). The combined driving force and process groups approach (d'Anterroches *et al*., 2005) has been used to design the solvent-based extractive distillation schemes. According to the method of d'Anterroches *et al*., (2005), for a solvent based extractive distillation process group, the minimum energy separation scheme can be achieved if a driving force of 0.48 is used. Using the ICAS-ProCamd tool from the ICAS software, among many other solvents, ethylene glycol and glycerol have been identified as matching the target driving force. Ethylene glycol has been selected because it is a known solvent for extraction of ethanol while glycerol is a by-product from the glucose fermentation. They confirm that the driving force target of 0.48 can be attained with an ethylene glycol fraction of 0.52 and with a glycerol fraction of 0.64.

2.3.2 Life cycle assessment and Economic analysis

The sustainable future of the world challenges engineers to develop chemical process designs that are not only technically and economically feasible but also environmental friendly. Life cycle assessment (LCA) is a tool for identifying and quantifying environmental impacts of the chemical product and/or the process that makes it. It can be used in conjunction with process simulation and economic analysis tools to evaluate the design of any existing and/or new chemical-biochemical process and to propose improvement options in order to arrive at the best design among various alternatives. Although there are several commercial LCA tools, there is still a need for a simple LCA software that can be integrated with process design tools.

In order to compare different technological alternatives any chemical processes, life cycle assessment (LCA) approach was used. LCA allows the compilation and evaluation of the inputs, outputs, and the potential environmental impacts of a product system throughout its life cycle. LCA is usually employed to highlight possible improvements in the production chain. In the work from Ojeda et al., 2010, LCA was applied to each case using SimaPro software (Eco-indicator99 method). The results show the highest effect on climatic change for second generation bioethanol production using the selected topologies (Figure 2.12). The Case3 showed the lowest total environmental impact but higher over human health and respiratory effects. The highest environmental impact was observed in Case 4 (Organosolv+SSCF) because of energy consumption and precipitated lignin. Impacts over ecosystem quality were observed in all cases. Waste treatment technologies and mass recycle strategies are recommended to reduce the environmental impact for these processes. Once, heat exchanger network are important to diminish the external energy supply for these technologies.

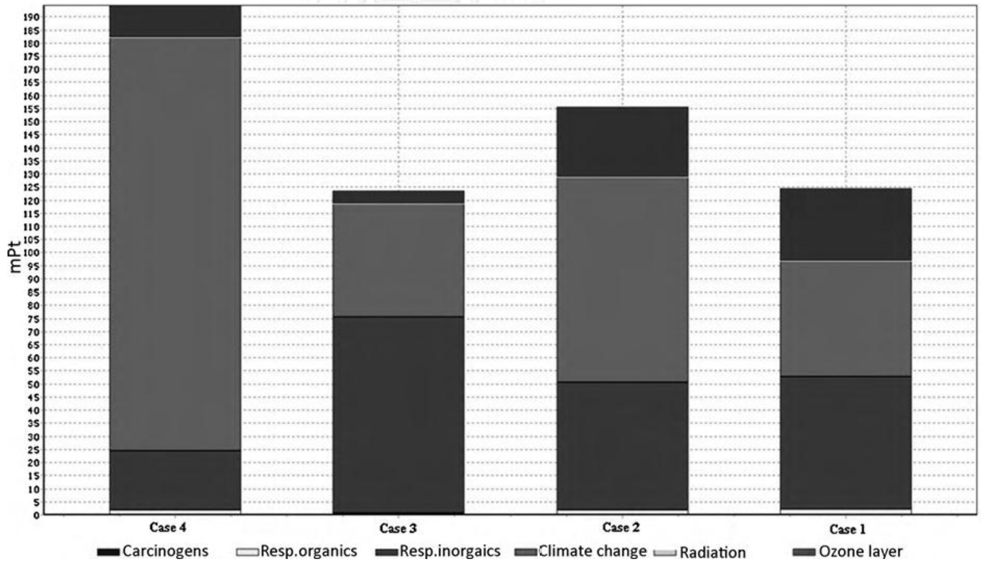


Figure 2.12 - Main LCA results. (modified from Ojeda et al., 2010)

For more reviews of the LCA issues, New et al., (2010) presents an approach integrating LCA indicators and dynamic simulation for green supply chain design and operation. Environmental impact indicators are incorporated into a dynamic model of the supply chain along with profit and customer satisfaction, so that sustainability of various design and operational decisions can be assessed comprehensively. LCA is one suitable tool for analyzing the environmental burdens associated with the design and operation of a SC (Bojarski et al., 2009). By using the ‘cradle to grave’ approach of LCA, each entity of the supply chain including suppliers, manufacturers, distributors/retailers and customers can be similarly identified with products, processes and/or transport activities which require material and energy and emit pollutants. This is illustrated using Figure 2.13 which shows the environmental impacts of a metal-working lubricant SC involving suppliers, the manufacturer and customers. Traditionally, the SC performance is measured only in terms of economic indicators such as profit and customer satisfaction.

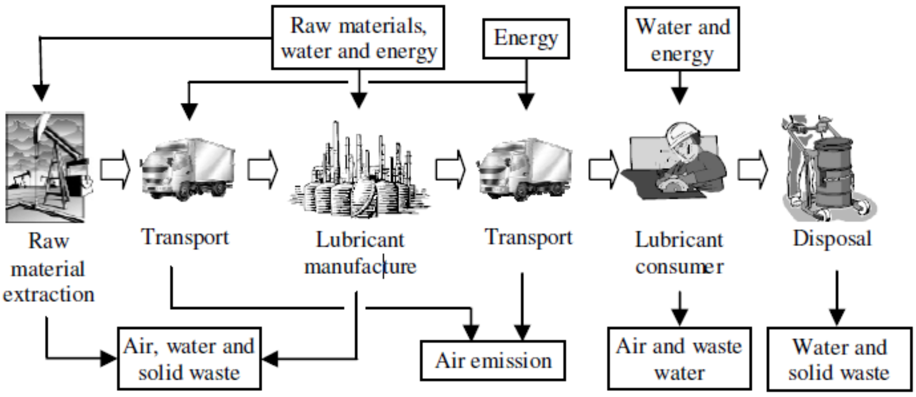
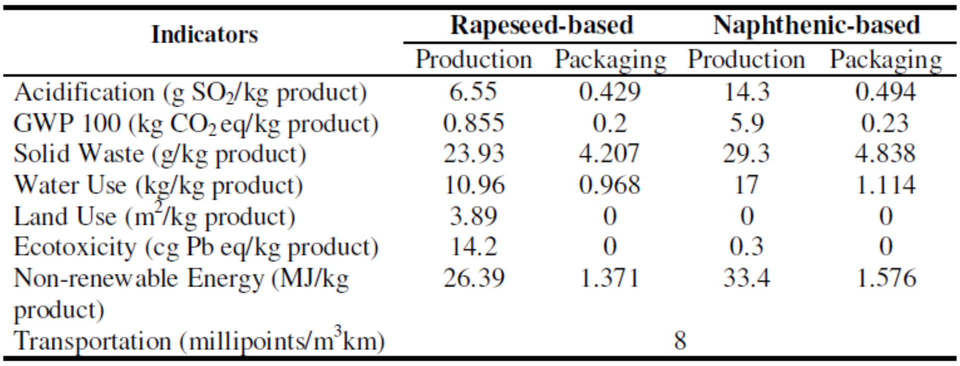


Figure 2.13 - LCA of a metal-working lubricant supply chain

Environmental impact indicators on the basis of the amount of products produced. Eight indicators are used, taking into consideration raw material acquisition, processing, packaging, and transportation from the plants to customers. These are acidification, global warming potential over 100 years (GWP 100), solid waste, water use, land use, ecotoxicity, non-renewable energy consumption, and transportation. These indicators are incorporated into the SC simulation model. This work focuses on two types of metal-working lubricants, one mineral-based (naphthenic oil) and the other bio-based (rapeseed oil). The lubricants are composed of the base oil, anionic surfactant and non-anionic surfactant. They make up about two percent of the metal-working fluid while the balance would be a carrier which can either be water, gaseous air or carbon dioxide. Since environmental concerns usually are far more significant for the lubricants rather than the carrier, we exclude the carriers in our subsequent analysis. Table 1 lists the indicator values per kg product for the two lubricants. The production indicators cover the impact from the raw material extraction stage up to the processing stage, for the production of 1 kg of lubricant (Clarens et al., 2008). We assume that the packaging used is 200L plastic drums made of high density polyethylene. The whole life cycle of the drum is considered during the calculation of packaging impact to the environment. The indicators for packaging (per kg of products packaged) in Table 1 are calculated based on Manuilova (2003). Transportation of packaged products is assumed to be done by 28-tonne trucks and the corresponding indicator is taken from Goedkoop et al. (2000). The indicators in Table 1 have been incorporated into the SC simulation model. The total impact for each indicator is the sum of the production and packaging impacts, calculated based on the mass of products produced. This total impact is then normalized based on the total mass of product produced of both lubricant types.

Table 2.8 - Environmental impact indicator values



Indicators	**Rapeseed-based**		**Naphthenic-based**	
	Production	Packaging	Production	Packaging
Acidification (g SO_2/kg product)	6.55	0.429	14.3	0.494
GWP 100 (kg CO_2 eq/kg product)	0.855	0.2	5.9	0.23
Solid Waste (g/kg product)	23.93	4.207	29.3	4.838
Water Use (kg/kg product)	10.96	0.968	17	1.114
Land Use (m^2/kg product)	3.89	0	0	0
Ecotoxicity (cg Pb eq/kg product)	14.2	0	0.3	0
Non-renewable Energy (MJ/kg product)	26.39	1.371	33.4	1.576
Transportation (millipoints/m^3km)	8			

The LCA software, LCSoft (Kalakul *et al.*, 2014), is developed for evaluation of chemical, petrochemical, and biochemical processes with options for integration with other process design tools such as sustainable design (SustainPro) (Carvalho *et al.*, 2013), economic analysis (ECON) (Saengwirun, 2011) and process simulation. To test the software, a bioethanol production process using cassava rhizome is employed as a case study as represented in Figure 2.14. The main user interface of tools integration is shown in Figure 2.9 which can combine the economic analysis and life cycle assessment. Results from LCSoft highlight the estimated environmental performance in terms of various aspects such as carbon footprint, resource and energy consumptions, and various environmental impacts as shown in Figure 2.15.

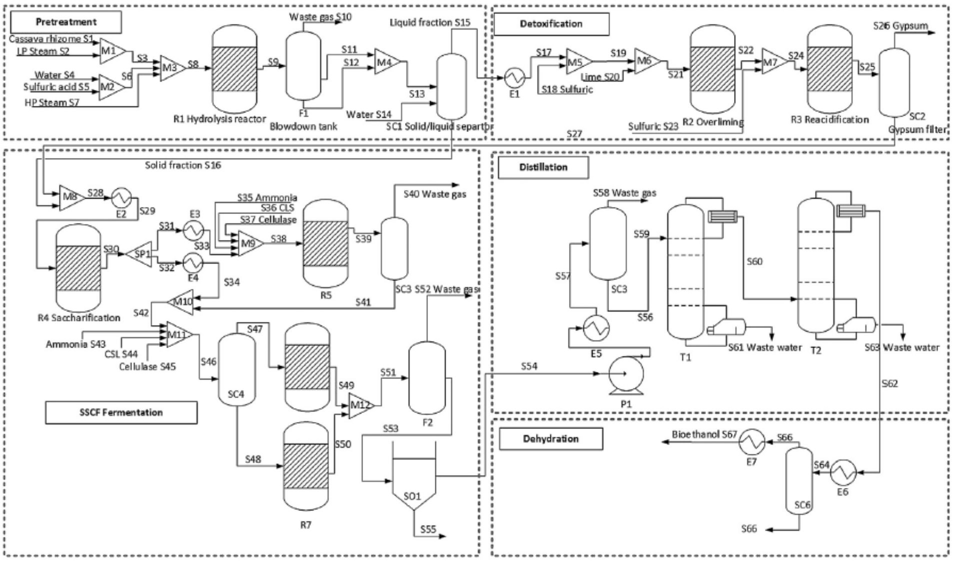


Figure 2.14 - Flowsheet of the case and LCA boundaries of the case study.

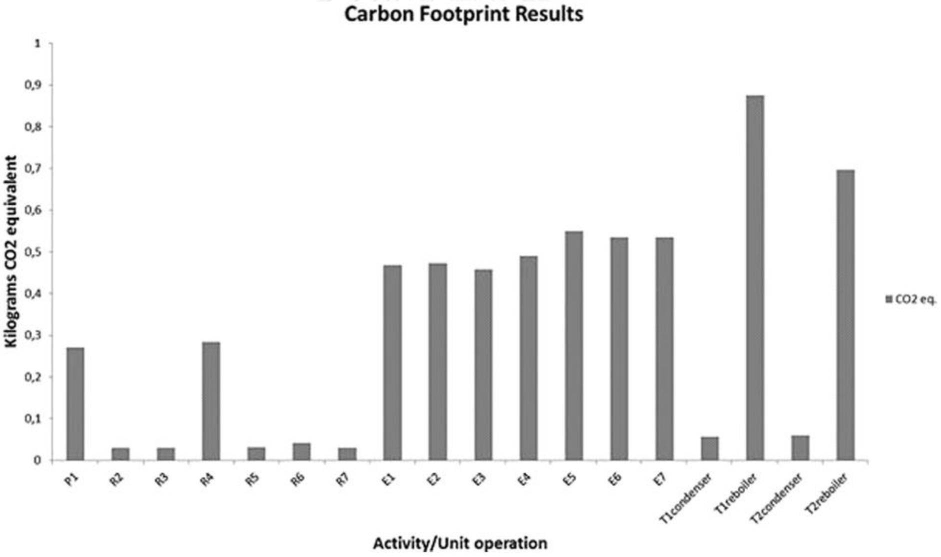


Figure 2.15 - Carbon footprint results.

2.3.3 Optimal processing route problem

This example addresses the optimal design of petrochemical SCs taking into account economic and environmental concerns and considering different sources of uncertainty affecting the environmental assessment of the process. Grossmann & Guillén-Gosálbez (2010) consider a superstructure based on a three-echelon SC (production-storage-market) with different available production technologies for plants, potential locations for SC entities and transportations links (see Figure 2.16). The goal is to maximize the NPV of the SC and minimize its environmental impact.

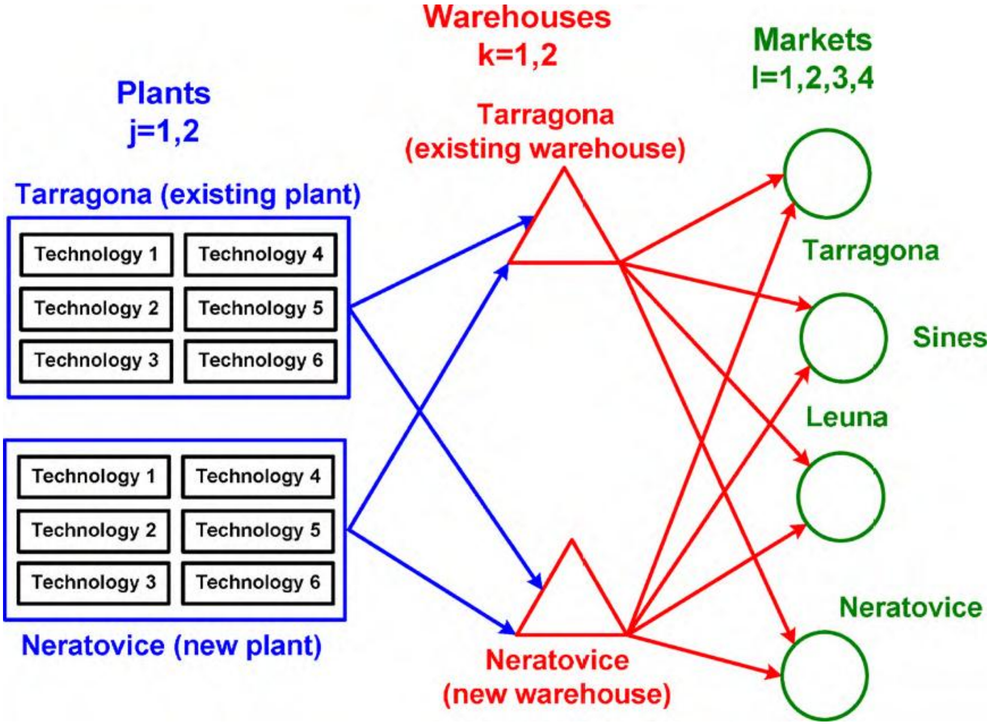


Figure 2.16 - Superstructure of example.

Moreover, the superstructure generation can applied in any chemical processes. The work from Zondervan *et al*., (2011) propose a biorefinery optimization model that can be used to find the optimal processing route for the production of ethanol, butanol, succinic acid and blends of these chemicals with fossil fuel based gasoline. The approach unites transshipment models with a superstructure, resulting in a Mixed Integer Non-Linear Program (MINLP). Consider a specific problem based on a network of 72 processing steps as represent in Figure 2.17 (including different pretreatment steps, hydrolysis, fermentation, different separations and fuel blending steps) that can be used to process two different types of feedstock. Numerical results are presented for four different optimization objectives (maximize yield, minimize costs, minimize waste and minimum fixed cost), while evaluating different cases (single product and multi-product).

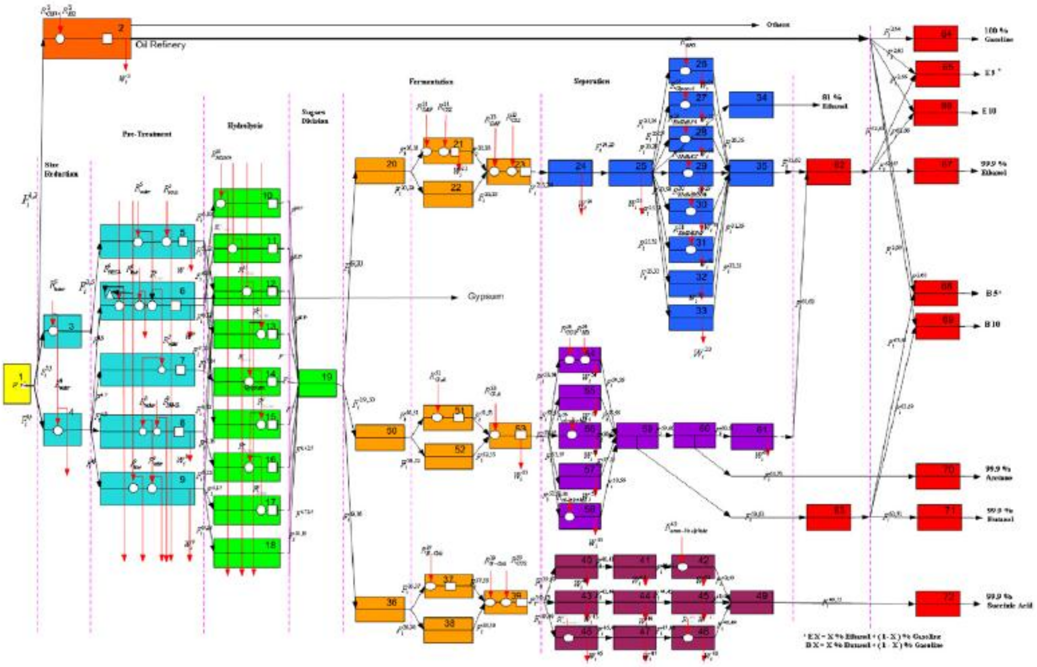


Figure 2.17 - Super structure of the biorefinery model. (modified from Zondervan *et al*., 2011).

The synthesis and design of processing networks is a complex and multidisciplinary problem, which involves many strategic and tactical decisions at business (considering financial criteria, market competition, supply chain network, etc.) and engineering levels (considering synthesis, design and optimization of production technology, R&D, etc.), all of which have a deep impact on the profitability of processing industries was proposed by Quaglia *et al*., (2012, 2013).

In Quaglia *et al*., (2012), study an integrated business and engineering framework for synthesis and design of processing networks is presented. The framework employs a systematic approach to manage the complexity while solving simultaneously both the business and the engineering aspects of problems, allowing at the same time, comparison of a large number of alternatives at their optimal points. The results identify the optimal raw material, the product portfolio and select the process technology for a given market scenario together with the optimal material flows through the network and calculate the corresponding performance and sustainability metrics.

The framework includes a software infrastructure for integrating different methods and tools needed for problem definition, formulation and solution of the design problem as a MINLP, reducing thereby the time and cost needed to generate and solve the design/synthesis problems and providing efficient data transfer between the tools. A generic structural process model has been implemented within the framework to describe the multidimensional engineering issues allowing thereby fast and flexible model development for various production processes. A case study from vegetable oil industry (Soy bean production as represented in Figure 2.18) is used successfully to demonstrate the applicability of the integrated framework for making optimal business and engineering decisions.

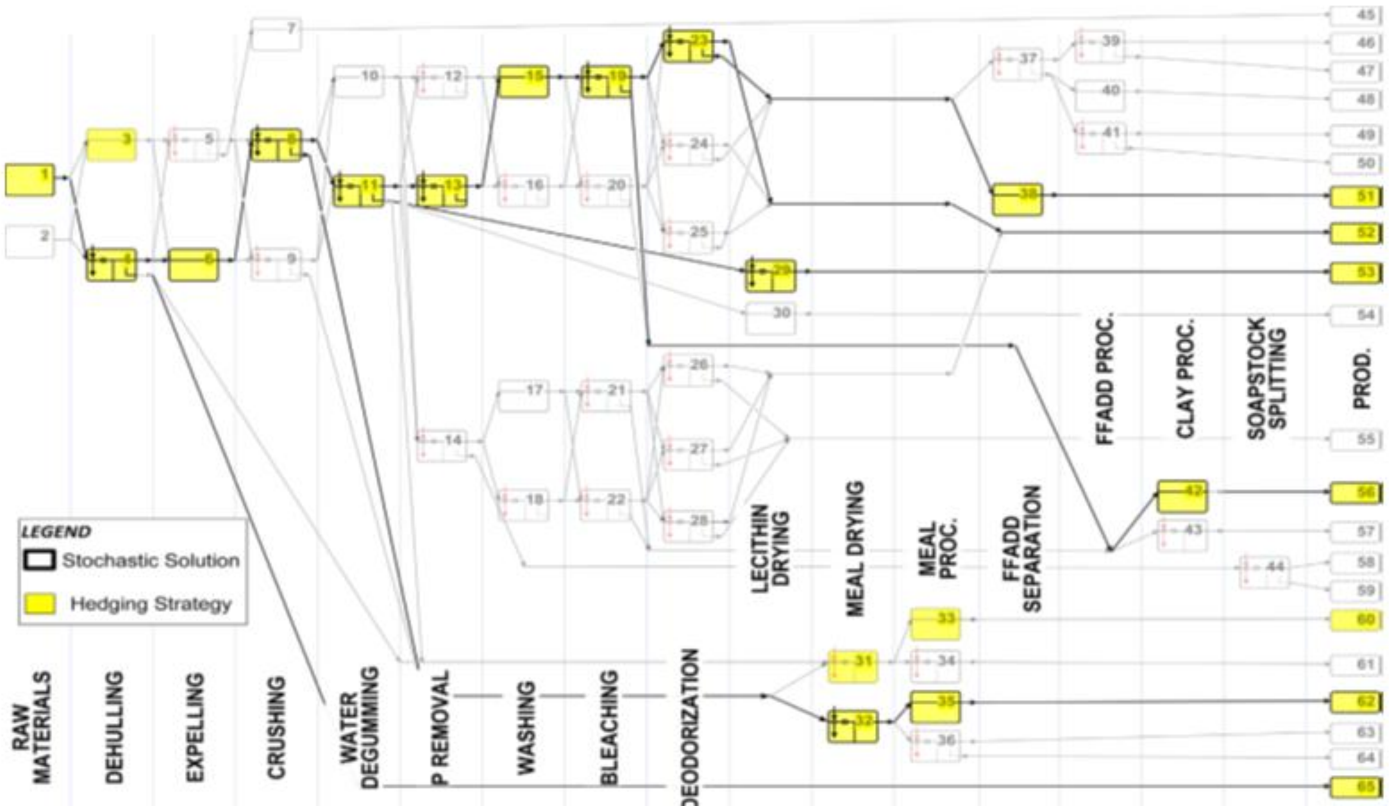


Figure 2.18 - Soybean oil processing network solution. In bold the optimal stochastic solution, in yellow the flexible network. (modified from Quaglia *et al*., 2012)

2.3.4 Process intensification: Phenomena based synthesis

Process intensification (PI) has the potential to improve existing processes or create new process options, which are needed in order to produce products using more sustainable methods. In principle, an enormous number of process options can be generated but where and how the process should be intensified for the biggest improvement is difficult to identify. The development of a systematic computer aided model-based synthesis and design methodology incorporating PI is presented by the work from Lutze et al., (2012).

Application of each step of the phenomena based synthesis framework is highlighted through a case study involving the production of dimethyl carbonate (DMC) which is an important bulk chemical due to its multiplicity of uses, from propylene carbonate (PC) and methanol (MeOH) with propylene glycol (PG) as a byproduct which was proposed by Babi *et al*., (2015). A selected process and simulated base case design is represented in Figure 2.13 and a brief description about the process is as follows. The raw materials, MeOH and PC, are fed at a mole ratio of 5:1, with MeOH in excess, to the reactor. In the reactor a transesterification reaction occurs to produce DMC and PG. The reactor outlet (effluent) consists of a multi-component mixture of MeOH, PC, DMC and PG. A minimum boiling azeotrope exists between MeOH/DMC. The first distillation column (T1) separates PC and PG (bottom of T1) from the reactor effluent. The top of T1 contains MeOH and DMC. The top stream of T1 is separated using pressure swing distillation, that is, the use of two distillation columns, (T2 and T3). The feed composition of MeOH and DMC entering T2 at the column pressure of 10 bar is to the left hand side of the azeotrope, therefore, high purity DMC is obtained as the bottom product of T2 and the top product of T2 is the MeOH/DMC azeotrope. The feed composition of MeOH and DMC entering T3 at the column pressure of 1 bar is to the right hand side of the azeotrope, therefore, MeOH is obtained as the bottom product. The recovered MeOH is recycled to the reactor and the top product is the MeOH/DMC azeotrope. In T4, PG is separated from PC. The recovered PC is recycled to the reactor.

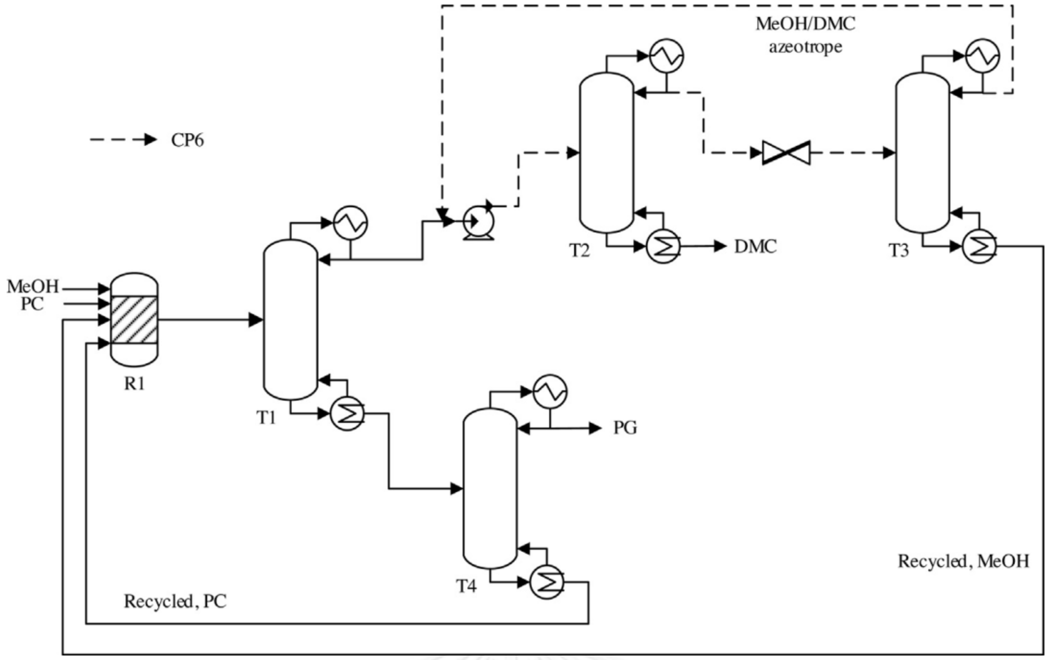


Figure 2.19 - Selected and simulated base case design. The closed path (CP) from the sustainability analysis is also highlighted.

An economic, sustainability and LCA analysis are performed. The sustainability analysis is shown in Figure 2.19 where the most critical stream (path) are highlighted and listed in Table 2.10. The LCA analysis and utility cost distribution (obtained from the economic analysis) are shown in Figure 2.14(a) and (b) respectively. From Table 2.10, CP6 which follows the raw material MeOH, has a high EWC. This translates into a high flow of MeOH being recycled within this path, resulting in high loads of energy and waste/use of utilities. From Figure 2.20, the unit operations belonging to this closed-path are T2 and T3. From LCA analysis, T2 and T3 also have high carbon footprints, that is, the reboiler of these two columns account for 30% and 15% of the utility costs.

Table 2.9 - Closed Path (CP6, see Figure 2.13) that has the highest potential for improvement.

Path	Compound	Flowrate (kg/h)	MVA (10^3\$/year)	TVA (10^3\$/year)	EWC (10^3\$/year)
CP6	MeOH	761.83	-	-	10253

The identified process hot-spots are given in Table 2.11: The design targets to be set/met are:

- Reduce energy consumption
- Reduce utility cost
- Improvements in LCA/sustainability indicators
- Unit operations reduction
- Product purity (kept as the base case)
- Production target (kept as the base case)
- Reduce operational cost
- Waste minimization

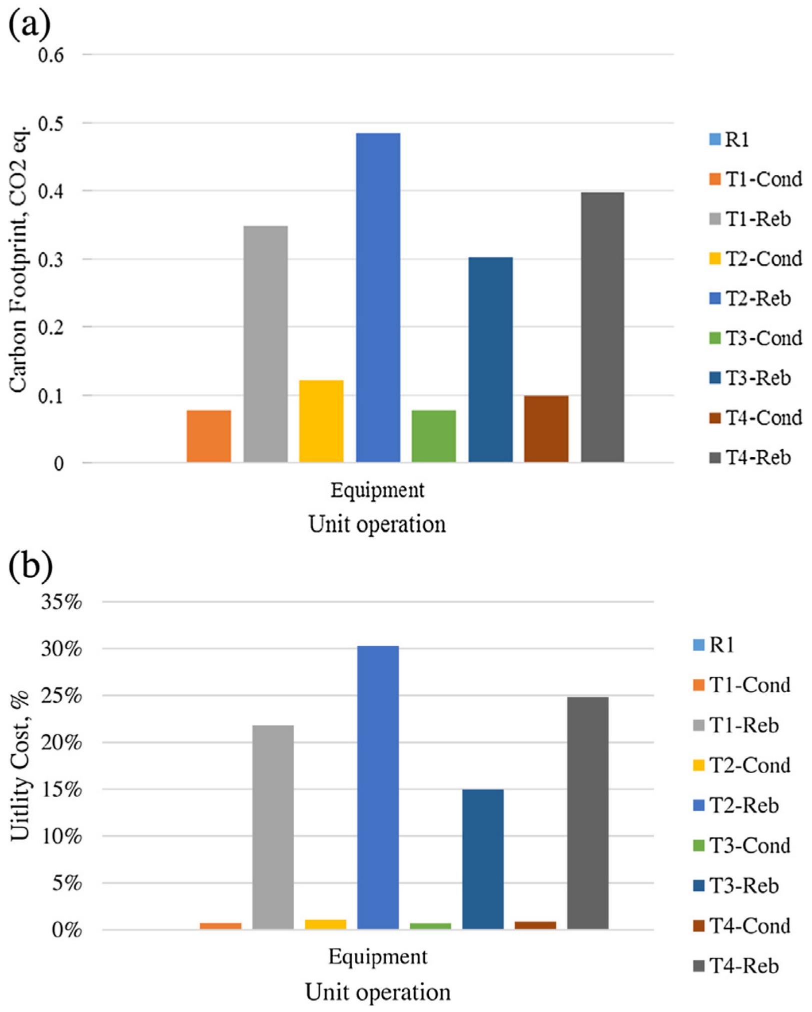


Figure 2.20 - (a) LCA analysis; (b) utility cost distribution. (Cond-condenser; Reb-reboiler).

Table 2.10 - Identified process hot-spots for the base case design.

Indicator values	Base case property	Cause	Identified process hot-spot
α_1 – raw material cost **β_1** – material value added	-Un-reacted raw materials	-Equilibrium reaction	-limiting equilibrium/raw material loss
α_2 – utility cost **β_1** – material value added **β_2** – Energy waste cost **γ_1** – CO_2 equivalent **γ_2** – Potential environment impact	-Un-reacted raw materials -Product recovery	-Presence of azeotrope(s) -High energy usage (heating/cooling)	-Azeotrope -Difficult separation due to low driving force -high energy consumption/ demand

Then the process base flowsheet was transform into task- and phenomena- based flowsheet as represented in Figure 2.21 and Figure 2.22, respectively.

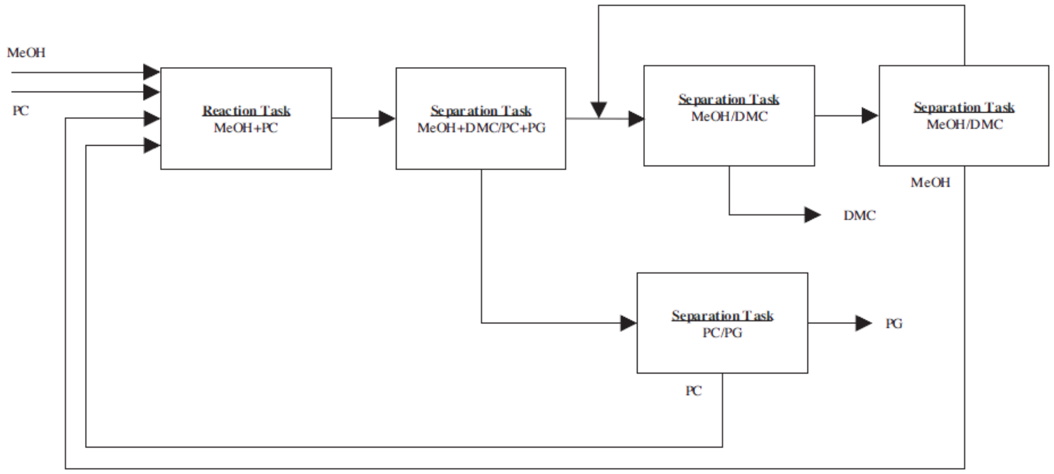


Figure 2.21 - Task based flowsheet of the base case design.

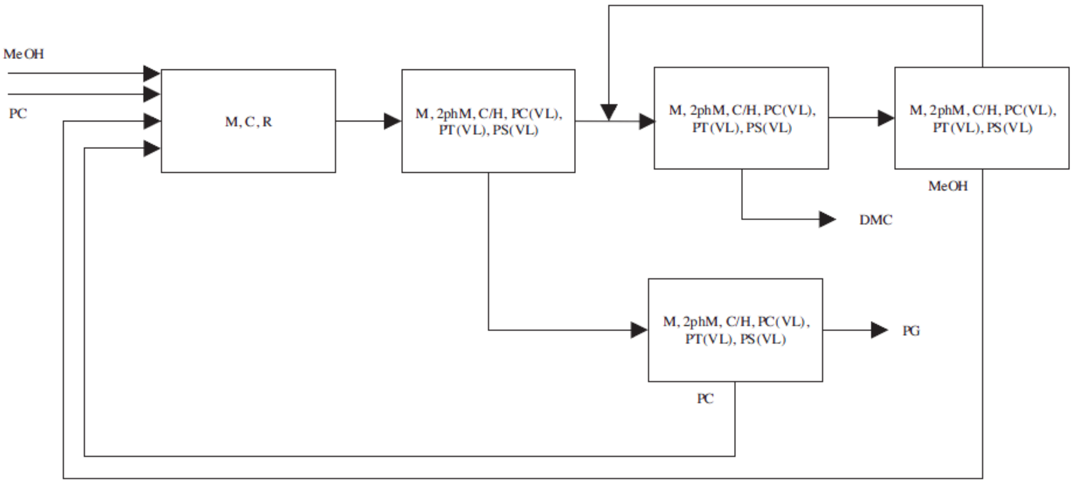


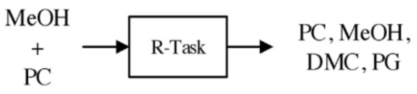
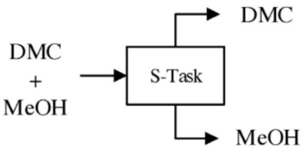
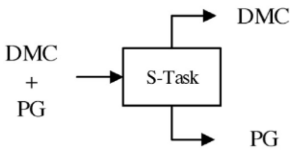
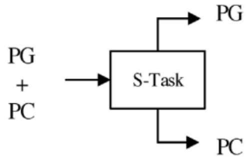
Figure 2.22 - Phenomena based flowsheet of the base case design.

From phenomena based flowsheet, the partial list of feasible simultaneous phenomena building blocks (SPBs) were generated as shown in Table 2.12. Each SPBs were using as basic structure then combine/integrate into task- based flowsheet in Table 2.13.

Table 2.11 - Partial list of feasible SPBs. Mix. – mixing, Cool. – cooling, Heat. – heating, React. – reaction, Sep. – separation, Ph. Cr. – phase creation, Div. – dividing. (modified from Babi *et al*., 2015).

SPB	Connected PBB	In	Out	Task they may perform
SPB.1	M	1 . . . *n*(L,VL,V)	1(L,VL,V)	Mix.
SPB.2	M – 2phM	1 . . . *n*(L,VL,V)	1(L,VL,V)	Mix.
SPB.3	M – R	1 . . . *n*(L,VL,V)	1(L,VL,V)	Mix. + React.
SPB.4	M – H	1 . . . *n*(L,VL,V)	1(L,VL,V)	Mix. + Heat.
SPB.5	M – C	1 . . . *n*(L,VL,V)	1(L,VL,V)	Mix. + Cool.
SPB.6	M – R – H	1 . . . *n*(L,VL,V)	1(L,VL,V)	React. + Heat.
SPB.7	M – R – C	1 . . . *n*(L,VL,V)	1(L,VL,V)	React. + Cool.
SPB.8	M – R – H – PC(VL) – PT(VL)	1 . . . *n*(L,VL,V)	1(L,VL,V)	React. + Heat.
SPB.9	M – R – C – PC(VL) – PT(VL)	1 . . . *n*(L,VL,V)	1(L,VL,V)	React. + Cool.
SPB.10	M – R – 2phM – PC(VL) – PT(VL)	1 . . . *n*(L,VL)	2(V/L)	React. + Sep.
SPB.11	M – R – 2phM – PC(VL) – PT(VL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	React. + Sep.
SPB.12	M – R – 2phM – PC(VL) – PT(PVL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	React. + Sep.
SPB.13	M – R – H – 2phM – PC(VL) – PT(PVL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	React. + Sep.
SPB.14	M – R – C – 2phM – PC(VL) – PT(PVL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	React. + Sep.
SPB.15	M – 2phM – PC(VL) – PT(VL)	1 . . . *n*(L,VL)	2(V;L)	Mix. + Ph. Cr
SPB.16	M – 2phM – C – PC(VL) – PT(VL)	1 . . . *n*(L,VL)	2(V;L)	Mix. + Ph. Cr.
SPB.17	M – 2phM – H – PC(VL) – PT(VL)	1 . . . *n*(L,VL)	2(V;L)	Mix. + Ph. Cr.
SPB.18	M – 2phM – PC(VL) – PT(VL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	Mix. + Sep.
SPB.19	M – C – 2phM – PC(VL) – PT(VL) – PS(VL)	1 . . . *n*(L,VL)	2(V;L)	Cool. + Sep.
SPB.20	M – H – 2phM – PC(VL) – PT(VL) – PS(VL)	1 . . . *n*(VL)	2(V;L)	Heat. + Sep.
SPB.21	M – 2phM – PC(VL) – PT(PVL) – PS(VL)	1 . . . *n*(VL)	2(V;L)	Mix. + Sep.
SPB.22	M – 2phM – PC(VL) – PT(VV) – PS(VV)	1 . . . *n*(L,VL,V)	2(V;V)	Mix. + Sep.
SPB.23	M – 2phM – PT(VV) – PS(VV)	1 . . . *n*(V)	2(V;V)	Mix. + Sep.
SPB. . .	. . .	. . .	. . .	. . .
SPB.70	D	1(L;VL,V)	1 . . . *n*(L;V; VL)	Stream Div.

Table 2.12 - Identified basic structures that perform single or multiple tasks. (modified from Babi *et al*., 2015).

SPB*	**Basic Structure**	**Task Performed**
SPB.7	M(L)=R(L)=C	
SPB.2 SPB.5 SPB.18 SPB.19 SPB.20 SPB.21 SPB.23	M(VL)=2phM M(L)=2phM=PC(VL)=PT(PVL)=PS(VL) M(V)=C M(V)=2phM=PT(VV)=PS(VV) M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) *NB: Multiple basic structures perform the same task, that is the separation of a binary azeotrope, in this case MeOH/DMC*	
SPB.18 SPB.19 SPB.20	M(VL)=C=2phM=PC(VL)=PT(VL)=PS(VL) M(VL)=2phM=PC(VL)=PT(VL)=PS(VL) M(VL)=H=2phM=PC(VL)=PT(VL)=PS(VL) *NB: 1 basic structure performs multiple tasks. This hints at the merging of tasks*	 

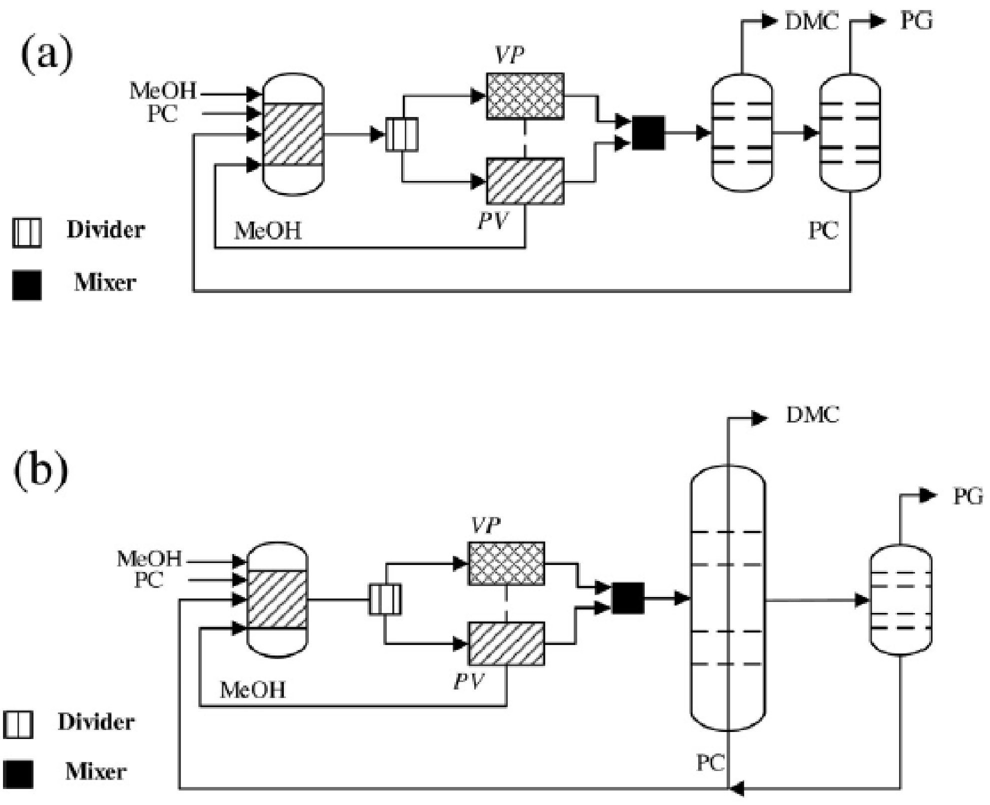
Use a database to translate the basic structures to tasks and then to unit operations. If the basic structure and its corresponding unit operation do not exist, then in principle, anew unit operation is generated. The list of unit operations are then screened based on the phase identity of the feed stream, use of a mass separating agent (MSA) and the presence of azeotropes with the data given in Table 2.14. The selected feasible unit operations are highlighted in bold in Table 2.14.

Table 2.13- List of identified unit operations based on identified basic structures for three cases: phase identity of feed stream; MSA and the presence of azeotropes.

SPB initiator in the basic structure	Task	Reaction/separation operation	Screening 1: feed phase	Screening 2: MSA-Y/N	Screening 3: azeotrope
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Partial condensation or vaporization	Vapor and/or liquid	N	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Flash vaporization	Liquid	N	N
=2phM = PC(VL) = PT(VL) = PS(VL)	**Separation**	**Distillation**	**Vapor and/or liquid**	**N**	**Y/N**
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Extractive distillation	Vapor and/or liquid	Y	Y/N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Reboiled absorption	Vapor and/or liquid	Y	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Stripping	Liquid	Y	N

=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Refluxed stripping (steam distillation)	Vapor and/or liquid	Y	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Reboiled stripping	Liquid	N	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Evaporation	Liquid	N	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Divided Wall Column	Vapor and/or liquid	N	N
=2phM = PC(VL) = PT(VL) = PS(VL)	Separation	Supercritical Extraction	Liquid	Y	N
=PC(VL) = PT(PVL) = PS(VL)	**Separation**	**Membrane-pervaporation**	**Vapor**	**N**	**Y**
=PC(VL) = PT(VV) = PS(VV)	**Separation**	**Membrane-vapor permeation**	**Vapor**	**N**	**Y**

The basic structures that perform the different identified tasks are translated into unit operations. The final flowsheet alternatives are presented in Figure 2.23 using a superstructure representation. In Figure 2.23(a), flowsheet alternative 2 uses a pervaporation membrane and flowsheet alternative 3 uses a vapor permeation membrane. In Figure 2.23(b), flowsheet alternative 4 uses a pervaporation membrane and flowsheet alternative 5 uses a vapor permeation membrane. In Figure 2.23(c) flowsheet alternative 6 is a single feed RD column with reactive stages only, flowsheet alternative 7 is a double feed RD column with reactive stages only, flowsheet alternative 8 is a single feed RD column with both reactive and non-reactive stages and flowsheet alternative 9 is a double feed RD column with both reactive and non-reactive stages.



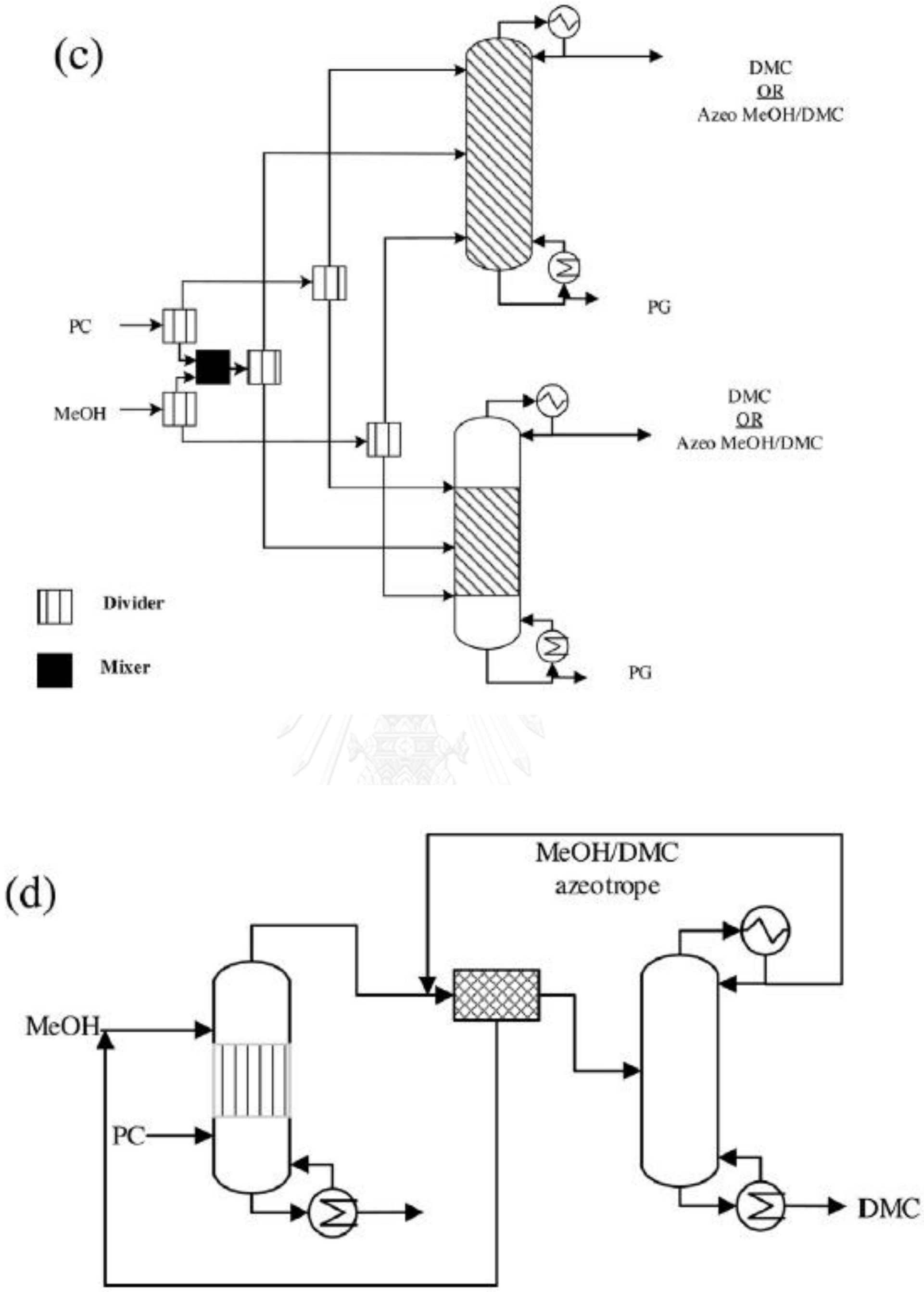


Figure 2.23 - The generated flowsheet alternatives for the production of DMC. (a) Flow-sheet alternatives 2–3, (b) flowsheet alternatives 4–5, (c) flowsheet alternatives 6–9,(d) flowsheet alternative 9. VP – vapor permeation membrane, PV – pervaporation membrane. (modified from Babi et al., 2015)

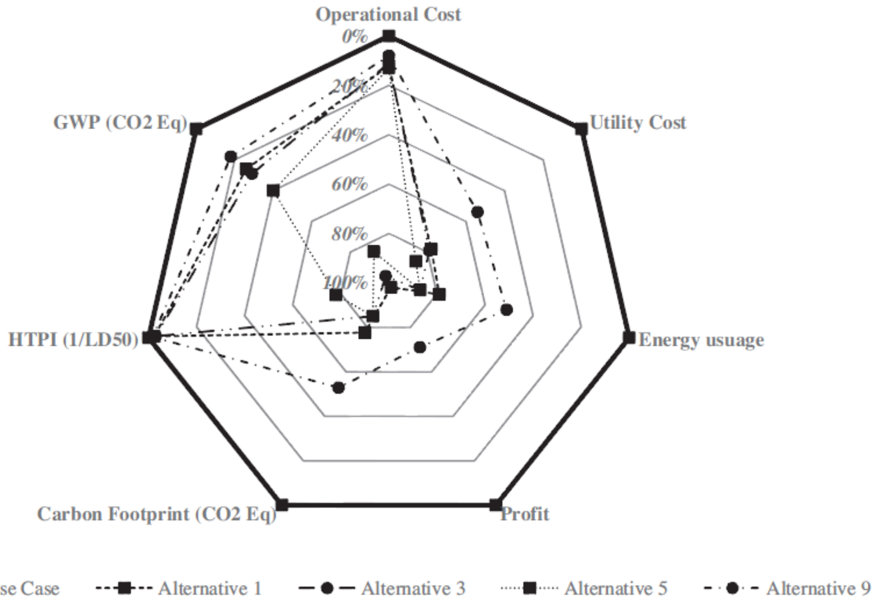


Figure 2. 24 - Economic and LCA improvements relative to the base case design per kilogram of DMC produced. (HTPI – Human Toxicity Potential by Ingestion, GWP – Global Warming Potential)

The results are represented in terms of a radar plot (Babi *et al.*, 2014). From Figure 2.24 it can be seen that for all the considered criteria, the alternatives are better that the base case design and therefore, non-tradeoff solutions have been obtained because the values of the indicators all lie within the radar plot. Reductions in energy consumption and utility cost have been achieved. The alternatives have a better value of the objective function compared to that of the base case design while showing improvements in the sustainability metrics and LCA factors. The numbers of unit operations for each alternative have been reduced for each alternative that is: 5 (base case), 4 (flowsheet alternative 3), 4 (flowsheet alternative 5) and 3 (flowsheet alternative 9). For each of the alternatives the product purity has been kept or improved while maintaining the production target. The operational cost of the alternatives showed improvement compared to the base case design and raw material lost has been minimized.

CHAPTER III
THEORY

3.1 Sustainable process design

Increased industrial activities combined with new economic environmental and societal constrains means that energy consumption, raw materials depletion and environmental impact are also receiving increased attention by modern society. Due to these factors, new as well as old industries need to achieve balance between the negative impacts from their activity and the positive benefits (due to the products they provide) to the society. In order to achieve a sustainable development, much progress is needed for the identification, design and development of appropriate products and processes that will produce them. For the industry to remain competitive and to adapt to the new realities of globalization, process improvements with respect to waste, environment, safety and cost are necessary. Therefore, it is useful to develop systematic methods and tools, which enable the generation of new more sustainable alternatives as well as ability to adapt to the future needs. In the past decades different methodologies have been proposed in order to determine the retrofit potential of a chemical process with respect to improvement of the cost-efficiency. Some methodologies were introduced using heuristic rules for the generation of the new design alternatives (Rapoport et al., 1994). Other methodologies based on mathematical concepts and optimization methods, such as mixed integer non-linear programming (MINLP) have also been proposed by Ciric and Floudas (1989) and Jackson and Grossmann (2002). Methodologies based on the resynthesize of the entire process by incorporating operating units with enhanced performance have been proposed by Liu et al., (2006). Finally, Lange (2002) has proposed a methodology that directly relates the process design alternatives to improvements in sustainability of the processes.

The objective of this chapter is to present theory on systematic methodology, which combines the process analysis which includes process generation, process selection and optimization by MINLP program to find “hot-spots” of the process, to debottleneck the process with the process intensification concept “phenomena based synthesis” and to evaluate in terms of sustainability metrics, economic and life cycle assessment in order to achieve the sustainable process design.

Starting first with how to find the optimal processing route and select a base case design for further analysis. The main idea of superstructure is to generate all of the possible processes (which are available) and specified scope of work. The process superstructure contains large amount of information of all process alternatives. The sets of raw materials, processing steps and products are used as process interval and combined together to establish “superstructure”.

Within the developed framework, the design space is represented by means of a stage-wise superstructure, as the one shown in Figure 3.1. Raw material alternatives are represented as first column of the superstructure, while product alternatives constitute the last column. The overall process, therefore, proceeds from the left to the right hand-side of the superstructure. The process to convert raw materials into products is represented as a sequence of process-steps, which are represented as columns of the superstructure. As the name indicates, each process-step constitutes a step in the transformation of raw materials into products. An example of process step is the removal of a given contaminant from a process stream. Each process-step contains one or more process-intervals (represented as boxes in the superstructure). A process-interval is defined as a technological alternative for the execution of a process-step. Examples of process-intervals for the above mentioned contaminant removal step, are separation via distillation, extraction, and selective conversion of the contaminant. Possible material flow patterns through the process-network are represented as connections between process-intervals, resulting in a network of process-intervals.

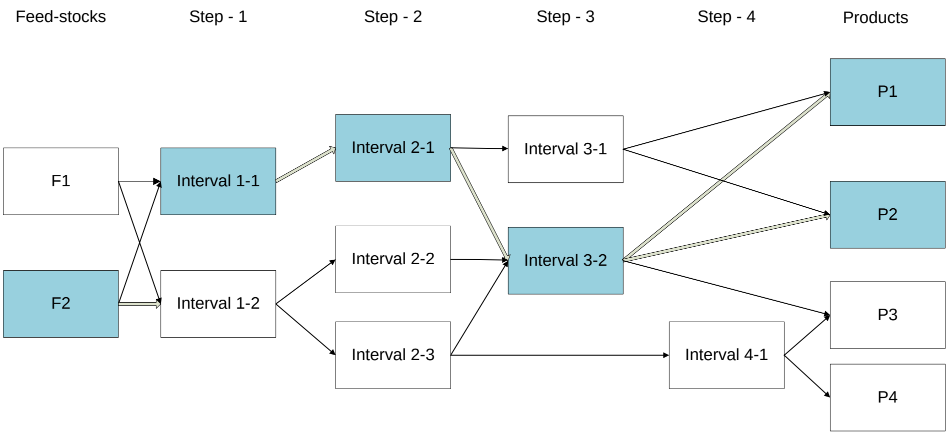


Figure 3.1 - Example of process superstructure.

Each process-interval is modeled as a sequence of elementary process-tasks, by formulating functional descriptors representing the transformation occurring to a stream in a generic manner such as mixing, utility dosage, reaction, stream division, separation and waste separation. The above described ontology constitutes the basis for the mathematical formulation of the optimization problem (reported in Table 3.1). After the MINLP solution, the optimal processing route is selected as base case design.

Table 3.1 - Mathematical formulation of the superstructure network (adapted from Quaglia *et al.*, (2013))

Raw material assignment	$F^{out}_{i,kk} = \phi_{i,kk}$	(3.1)
Utility consumption	$F^{M}_{i,kk} = \sum_{k} (F_{i,k,kk}) + \alpha_{i,kk} \cdot \mu_{i,kk} \cdot \sum_{i,k} (F_{i,k,kk})$	(3.2)
Reaction	$F^{R}_{i,kk} = F^{M}_{i,kk} + \sum_{rr,react} (\gamma_{i,kk,rr} \cdot \theta_{react,kk,rr} \cdot F^{M}_{react,kk})$	(3.3)
Waste separation	$F^{out}_{i,kk} = F^{R}_{i,kk} \cdot (1 - SW_{i,kk})$ $F^{WASTE}_{i,kk} = F^{R}_{i,kk} - F^{out}_{i,kk}$	(3.4) (3.5)
Product-product separation	$F^{out1}_{i,kk} = F^{out}_{i,kk} \cdot \sigma_{i,kk}; F^{out2}_{i,kk} = F^{out}_{i,kk} \cdot (1 - \sigma_{i,kk})$	(3.6)
Superstructure flow model	$F^{1}_{i,k,kk} \leq F^{out1}_{i,kk} \cdot \xi^{P}_{k,kk}; F^{2}_{i,k,kk} \leq F^{out2}_{i,kk} \cdot \xi^{S}_{k,kk}$ $\sum_{k} F^{1}_{i,k,kk} = F^{out1}_{i,kk}; \sum_{k} F^{2}_{i,k,kk} = F^{out2}_{i,kk}$	(3.7) (3.8)
Superstructure logic model	$F^{R}_{i,kk} \leq M \cdot y_{kk}$ $\sum_{j} (y_k \cdot v_{st,k}) \leq 1$	(3.9) (3.10)
Throughput limitation	$\sum_{i} F^{R}_{i,kk} \leq F^{MAX}_{kk}$	(3.11)
Piece-wise linear capital cost model	$CAPEX = \sum_{kk} \left[\sum_{j} (\alpha_{j,kk} \cdot w_{j,kk} + \beta_{j,kk} \cdot Q_{j,kk}) \right]$ $F^{Thr}_{kk} = \sum_{j} Q_{j,kk}; \sum_{j} w_{j,kk} = 1; \; Q^{o}_{j,kk} \cdot w_{j,kk} \leq Q_{j,kk} \leq Q^{o}_{j+1,kk} \cdot w_{j,kk}$	(3.12) (3.13)

After the optimal processing route was obtained from the MINLP solution. The process sustainable design is to design and synthesize the process to achieve the process flowsheet containing mass and energy balances. With the rigorous simulation and the completed flowsheet, the knowledge of chemical engineering based knowledge, heuristic rules, chemical plant design and process group (PG) contribution method were used to design and synthesize the process flowsheet.

The PG concept (d’Anterroches & Gani, 2005) following the principles of the group-contribution approach from chemical property estimation is applied to the synthesis and design of chemical process flowsheets. In a group-contribution method for pure component/mixture property prediction, a molecular identity is described by means of a set of groups bonded together to form a given structure. For flowsheet property prediction, a process flowsheet can be described by means of a set of process-groups bonded together to represent the flowsheet structure. The process-groups represent either a unit operation (such as reactor, distillation, and flash), or a set of unit operations (such as extractive distillation and pressure swing distillation). The bonds among the process-groups represent the streams and/or recycles, in an analogous way to the bonds that are attachments to molecular groups. Each process group provides a contribution to the property of the flowsheet. This property can be performance (in terms of energy consumption, operating cost, profit, etc.) defined in such a way that once the flowsheet is described by the process-groups, the flowsheet property can be calculated.

In the base case design, the reverse simulation method is the procedure by which knowledge of the values of the state variables of the inputs and outputs of a unit operation (i.e., individual flowrates, pressure and temperature) is used to calculate the design parameters of the corresponding unit operation (number of stages, feed location, reflux ratio, residence time, and volume) as the unknown variables from the process model.

Next is the rigorous process simulation of the base case design. In principle, any process simulator could be used. However, before a rigorous simulation can be performed, it is important to check if all the necessary data are available. The appropriate unit operation models together with the consistent thermodynamic models will need to be employed from the selected simulator. Then after the rigorous simulation was achieved, the process analysis was take place to finding the most potential points for further improvement in our process. The detail of process analysis is considered in section 3.2.

3.2 Process analysis

The process analysis for process improvement is to identify the most potential points for further improvement in the process or “hot-spots”. From the previous step (3.1), the base case design was obtained from rigorous process simulation. However, when considering the energy-mass-eco efficiency, these process performance indicators are still low. So, the need of process analysis tools plays essential role to find hot-spots in the process.

The algorithm and work-flow of process analysis are represented in Figure 3.2 which required the input of mass and energy balance in the process flowsheet (step 1) and decomposed the process flowsheet into material streams and energy streams in closed-path (CP) and open-path (OP) in step 2. Then after flowsheet decomposition step, the process performance indicators are analyzed in term of important issues

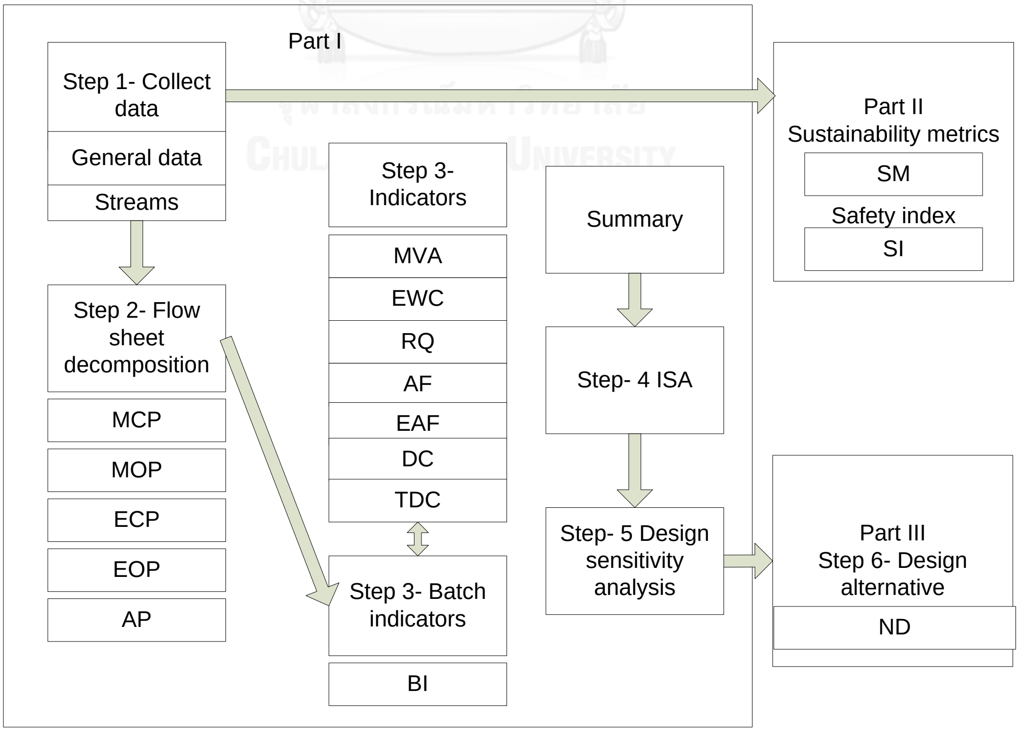


Figure 3.2 - Work-Flow of process analysis.

For more clarifying of the process analysis, the detail of SustainPro was described here. First, the user has to make the input of the mass and energy balance, along with the connectivity data among the different equipment. The software deconstructs the given mass and energy balances into open and closed paths. It is important to notice that a path represents a compound that follows a certain route; in terms of mass, a closed path means that a certain compound is being recycled in a given path, and an open path means that a compound is entering and leaving the system and that it is not being recycled.

The work-flow for the new extended methodology is organized in terms of six steps and is highlighted in the text below, each step is explained.

Step 1: Collect steady-state data

The objective of this step is to collect the mass and energy data corresponding to the steady-state operation of the process under investigation. This data can be provided as steady-state simulation results (for example, from commercial simulators like PROII® or ASPEN®) or operational data collected from the plant. Therefore, the methodology can be applied to any chemical process, for which steady-state operational data is available.

Step 2: Flowsheet decomposition

The objective of this step is to identify all the mass and energy flow-paths in the process by decomposing into open and closed-paths for each compound in the process. The closed-paths (cp) are the process recycles with respect to each compound in the process. In other words, they are the flow-paths which start and end in the same unit of the process. An open-path (op) consists of an entrance and an exit of a specific compound in the process. The entrance of the compound in the system can be due to its entrance through a feed stream or by its production in a reactor unit. The exit of the respective compound can be due to a “demand” (exit) stream or by its reaction in a reactor unit. Figure 3.3 highlights the main steps of the flowsheet decomposition algorithm.

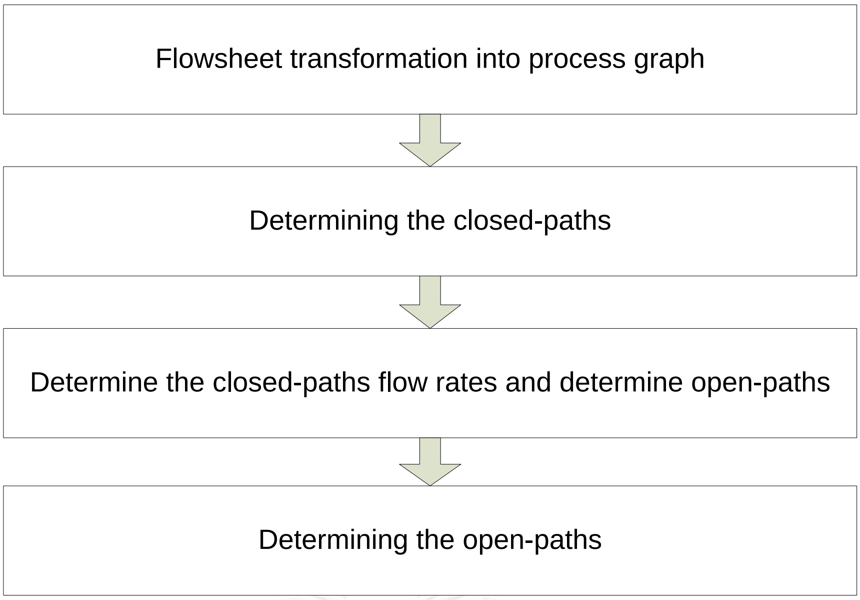


Figure 3.3 – Main steps for the flowsheet decomposition.

Step 2.1: Flowsheet transformation into a process graph

In this step, the flowsheet is transformed into a process graph, where the units are represented as vertexes and while the edges joining two vertexes are the streams. The edges are represented by arrows in order to give a direction to the flowrate sequence across the system. All the feed and demand (exit) streams are represented by bold arrows, including the compounds which enter and exit the system by reaction. More details about the transformation of the flowsheet into a process graph are given in Uerdingen *et al*. (2003).

Step 2.2: Determining the closed-paths

Before identifying the closed-paths within the flowsheet it is necessary to decompose the flowsheet into different partitions. The Sargent and Westerberg algorithm, Sargent and Westerberg (1964), is implemented here. With all the partitions identified, it is possible to determine the closed-paths within each partition using the algorithm described in Biegler *et al*. (1997).

Step 2.3: Determining the closed-paths flowrate and determine the open-paths

The flowrates associated to closed-paths, needs to be identified before the identification of the open-paths and their associated flowrates. This is because the mass accumulated in the cycles needs to be subtracted from the corresponding open-path streams. This allows defining a new graph only with the compounds amounts related with entrance and the exit of a given compound.

Each indicator represents an open or closed path and points to bottlenecks with respect to mass and/or energy that are wasted or that go around in a recycle loop (i.e., trapped and cannot get out). Therefore, the indicators indicate the potential for generating more sustainable solutions. A brief summary of the meaning of each indicator is listed in Table 3.2. The indicators with the highest potential are then designated as design targets for generation of new design alternatives. Based on the knowledge of the definition of the mass and energy indicators and on the general behavior of process systems, it is possible to qualitatively judge if it is feasible to make changes on the operational variables related to the targeted indicators.

Table 3.2- Mass and Energy Indicators Summary.

Indicator	Meaning
Material value added (MVA)	Value generated between the entrance and exit of a certain compound in a given path (if negative, it must be increased). A negative value of MVA means that the compound in that specific path is losing monetary value. Possible way of improving the process sustainability: recycle (implementation).
Energy waste cost (EWC)	Represents the maximum theoretical amount of energy that can be saved in each path, open or closed (if positive it must be decreased). A positive value of EWC means that, in a certain path, there is a large amount of energy being wasted, energy that is being added to the system, or energy produced in situ. Either way, a highly positive value represents possible sustainability improvement with heat integration.

Total value added (TVA)	Describes the economic influence that a compound has in a certain path. It is given by TVA, MVA, EWC (if this value is highly negative it must be increased). It could be the result of a negative MVA, a highly positive EWC, or a combination of both.
Reaction quality (RQ)	Measures the influence of a compound in a given path. The user must provide this information after performing an exhaustive evaluation on the compounds effect (in a certain path) on the process overall productivity. If negative, then the compound represents a negative impact on the process productivity; if zero, then it means that the compound has no impact on the process productivity; if positive, then it means that the compound is contributing positively to the system productivity. Possible way of improving the process sustainability and then decreasing the negative impact on the process productivity: implement purge to decrease the amount of compound on the system or improve the chemical synthesis.
Demand cost and total demand cost (DC and TDC)	Applied only to open paths once it tracks the energy flows across the system. DC represents the energy flow of a compound from the entrance to the exit. TDC represents the total energy flow for every compound in a certain path (both give a quantitative evaluation in monetary units per kg).

	For each path the user can evaluate the weight that a compound has on the global TDC value for a certain path.
Mass accumulation factor and energy accumulation factor (AF and EAF)	Applied only to closed paths once it describes/determines the accumulative behavior of a compound in that path (AF) or the accumulative behavior of the energy in that same path (EAF). Both are due to the amount that is being recycled relative to the input to the system. High values represent high possibility for improvements.

3.3 Process intensification

The process intensification is the concept of the improvement and innovation of the process, by based knowledge, heuristic rules, experience or innovative method. The objective of this step is to intensify our base case design, make the existing process better with the advance synthesis-design and meet the target setting such as improvement in energy efficiency, improvement reaction conversion and yield, reduce waste generation in the process and improvement of overall important performance indicators (economic and life cycle assessment). Four explicit goals of process intensification (PI): (1) maximize the effectiveness of intra- and intermolecular events; (2) optimize the driving forces at every scale and maximize the specific surface area to which these forces apply; (3) maximize synergistic effects, and (4) give each molecule the same processing experience. According to Van Gerven and Stankiewicz (2009), these goals can be achieved through four domains: structure, energy, synergy and time. However, since the desired behavior of a process or a unit operation is evaluated by its performance and attained by the interaction of the involved phenomena, the goals of PI are actually achieved by enhancements of the involved phenomena inside the four domains which will be described in this part.

The process design-synthesis–intensification problem is defined: For the production of a specified product, generate more sustainable process designs. These alternatives may include well-known, existing and novel hybrid/intensified unit operations that provide improvements in terms of efficient use of raw materials, sustainability metrics (impacts) as well as LCA factors compared to a reference (base case) design.

The mathematical description is given in Section A, the solution approach in Section B, the concept of performing process intensification at different scales in Section C and the criteria for sustainability and LCA are explained in Section D.

A. - The mathematical description

The problem definition for process synthesis–intensification is translated into a mathematical form:

$$\frac{min}{max f_{obj}^{o}} = f_{obj}^{o}(X, Y, d, z, \Theta) \tag{3.14}$$

Subject to:

$$g(X, z, \Theta) \tag{3.15}$$

$$f(X, Y, d, z, \Theta) = 0 \tag{3.16}$$

$$b^L \leq b_1 X + b_2 Y \leq b^U \tag{3.17}$$

$$h^L \leq h(X, Y, d, \Theta) \leq h^U \tag{3.18}$$

$$v^L \leq v(X, Y, d, \Theta) \leq v^U \tag{3.19}$$

$$w^L \leq w(X, Y, d, \Theta) \leq w^U \tag{3.20}$$

$$Y = \frac{0}{1}, X \geq 0 \tag{3.21}$$

The objective function (Eq. (3.14)) can be linear or non-linear, is dependent on a set of, design/optimization variables X-, binary (0,1) decision integer variables Y-, equipment (unit operations) parameters d-, thermodynamic variables z-, and *Θ*-, process and product specifications Eq. (3.14) represents the objective function to be minimized or maximized subject to a set of linear and non-linear constraints (Eqs. (3.15)–(3.21)). Eqs. (3.15) and (3.16) represent a system of linear and non-linear equations (constraints), representing the process models. Here, the process models are considered at steady state conditions only, consisting of the phenomena as well as mass and energy balances. Eqs. (3.17) and (3.18) represent the flowsheet physical constraints and equipment design specifications, for example, the process flowsheet structure and equipment boundaries, respectively. Eqs. (3.19) and (3.20) represents PI constraints, that is, intensification design specifications and performance criteria that the feasible flowsheet alternatives must satisfy for example, the inclusion of intensified (mature/novel) equipment within the search space of available unit operations and the improvement of sustainability/LCA factors, respectively. The process synthesis–intensification problem to be solved becomes a mixed integer non-linear programming (MINLP) problem because, as seen from Eqs. (3.14)–(3.20), the objective function and constraint scan be linear and non-linear and binary decisions must be made in selection between different phenomena/tasks/equipment for the generation of feasible flowsheet alternatives (Papoulias *et al*., 1983; Quaglia *et al*., 2012; Lutze *et al*., 2013).

B. - Solution approach: decomposition based solution strategy

In order to manage the complexity related to the solution of the MINLP synthesis-intensification problem, an efficient and systematic solution approach is needed. One approach (Karunanithi *et al.*, 2005), decomposes the problem into a set of sub-problems that are solved according to a pre-defined calculation order. Most of the sub-problems require bounded solution of a sub-set of equations and the final sub-problem is solved as a set of NLP or MILP. Therefore flowsheet alternatives are generated by simultaneously solving the process model equations, Eqs. (3.23) and (3.24), subject to the constraints defined in Eqs. (3.25) and (3.26). The objective function defined by Eq. (3.27) is calculated and ordered for the remaining feasible flowsheet alternatives. The generated alternatives are then assessed using a set of PI performance criteria specified in Eq. (3.28). The performance criteria are related to the performance and improvement in economic, sustainability and LCA factors, of the whole or part of the process through the application of hybrid/intensified unit operations (Lutze *et al.*, 2012; Babi *et al.*, 2014). The flowsheet alternative(s) that give the best objective function value are selected as the more sustainable process designs. Note that a direct solution of the MINLP problem is also possible (Zondervan *et al.*, 2011; Quaglia *et al.*, 2013).

C. - Phenomena-based synthesis and a comparison to CAMD

Phenomena-based synthesis is defined as the generation of more sustainable designs from the combination of phenomena building blocks (PBBs) at the lowest scale (phenomena) that perform a task at the higher scale (task). Therefore, in performing phenomena-based synthesis, PBBs are combined to form simultaneous phenomena building blocks (SPBs) that are combined to form basic structures that perform a task or set of tasks, using pre-defined rules. These basic structures are then translated in to unit operations (highest scale) that constitute the final flowsheet alternatives. The combination of PBBs to generate basic structures is rule based and analogous to CAMD (Harper *et al.*, 2000) where atoms are combined to generate functional groups that are combined to form molecules with a set of desired properties (performance criteria). The comparison of phenomena-based synthesis to CAMD is shown in Figure 3.4.

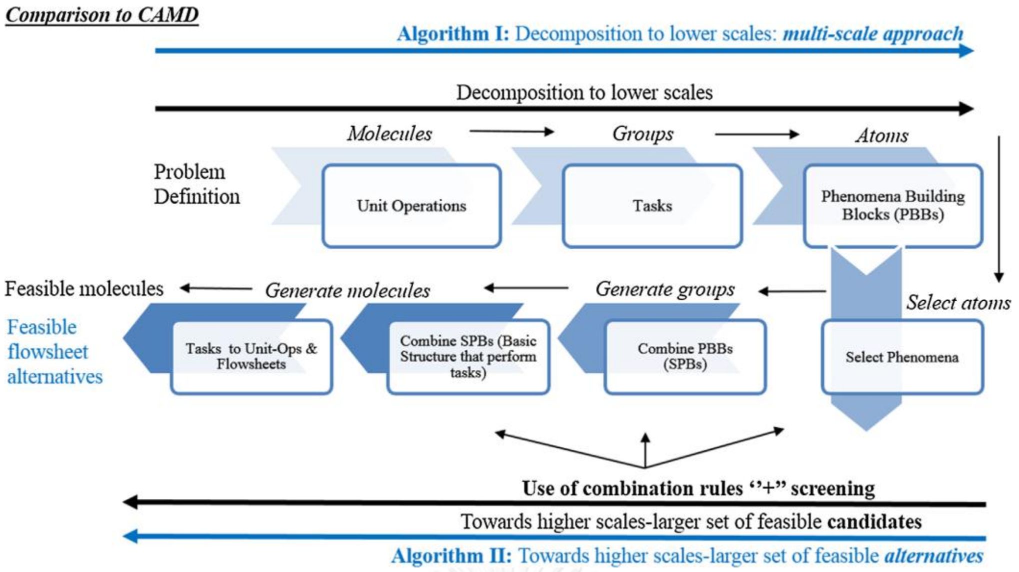


Figure 3.4 - A comparison of phenomena-based synthesis to CAMD. (modified from Babi *et al*., 2015).

- Phenomena based synthesis

C.1. - Phenomena building blocks and simultaneous phenomena building blocks

A phenomena building block (PBB) is considered in this work as the smallest unit that performs a task in a process. For example, a mixing PBB performs a mixing task. A simultaneous phenomena building block (SPB) is defined as the combination of one or more phenomena building blocks using predefined combination rules. Most chemical processes can be represented by different combinations of mass, energy and momentum transfer phenomena (Lutze *et al*., 2013) such as mixing (M), two-phase mixing (2phM),heating (H), cooling (C), reaction (R), phase contact (PC), phase transition (PT) phase separation (PS) and dividing (D). A "dividing" phenomena divides a stream into one or more streams. Each PBB contributes to mass and energy balances that are solved for the system boundary of the SPB. The inlet/outlet stream states of the PBBs are liquid (L), vapor (V), solid(S) and/or their combinations, for example, vapor and liquid (VL), liquid–liquid (LL), vapor–liquid–liquid (VLL), and solid–liquid (SL). It should be noted that all possible combinations of SPBs are obtained from the combinations of the 9 PPBs listed above. The 9 individual phenomena building blocks are used in the generation of feasible SPBs using the following rules:

- M – If separation or reaction is occurring, mixing of the compounds in the separating mixture and/or mixing of the reactants occur therefore, a “M” PBB is required;
- R – If a reaction is occurring, raw materials are converted to products, therefore, a “R” PBB is required;
- 2phM – If separation or reaction is occurring in a two phase system, mixing of the two phases occur therefore, a “2phM” PBB is required;
- PC – If two phases are present then, contact of between the two phases occur therefore, a “PC” PBB is required;
- PT – If two phases are present then transition from one phase to the other occur, for example, consider a vapor-liquid system where liquid “transitions” into vapor due to heating and vapor “transitions” into liquid due to cooling. When this occurs a “PT” PBB is required;
- PS – If two phases are present then separation of the two phases occur therefore, a “PS” PBB is required;
- H/C – If a single phase or multiple phases are present and there are changes in enthalpy due to internal and/or external energy sources then a “H” or “C” PBB is required;
- D – If the dividing of streams is needed then a “D” PBB is required.

Figure 3.4(a)–(c) highlights the representation of three different unit operations in terms of SPBs that are formed by combination of PBBs. This is explained as follows:

- Flash vessel (phases: vapor and liquid) – In the flash vessel the following are occurring simultaneously, mixing plus two phase mixing, phase contact between vapor and liquid, transition from one phase into another and the separation of two phases. Therefore, the following PBBs are required in order to generate feasible SPBs that represent the flash vessel, M, 2phM, PC(VL), PT(VL),PS(VL) as highlighted in Figure 3.5(a);
- Distillation column (phases: vapor and liquid) – In the distillation column, the same PBBs as the flash vessel are selected plus heating and cooling PBBs for properly representing the condenser and reboiler. The following PBBs are required in order to generate feasible SPBs that represent the distillation column, M, 2phM,PC(VL), PT(VL), PS(VL), H, C as highlighted in Figure 3.5(b);

- Reactive distillation (phases: vapor and liquid) – In the reactive distillation column, the same PBBs as the distillation column are selected plus reaction because reaction and separation are also occurring simultaneously. The following PBBs are required in order to generate feasible SPBs that represent the reactive distillation column, M, 2phM, PC(VL), PT(VL), PS(VL), H, C, R as highlighted in Figure 3.5(c).

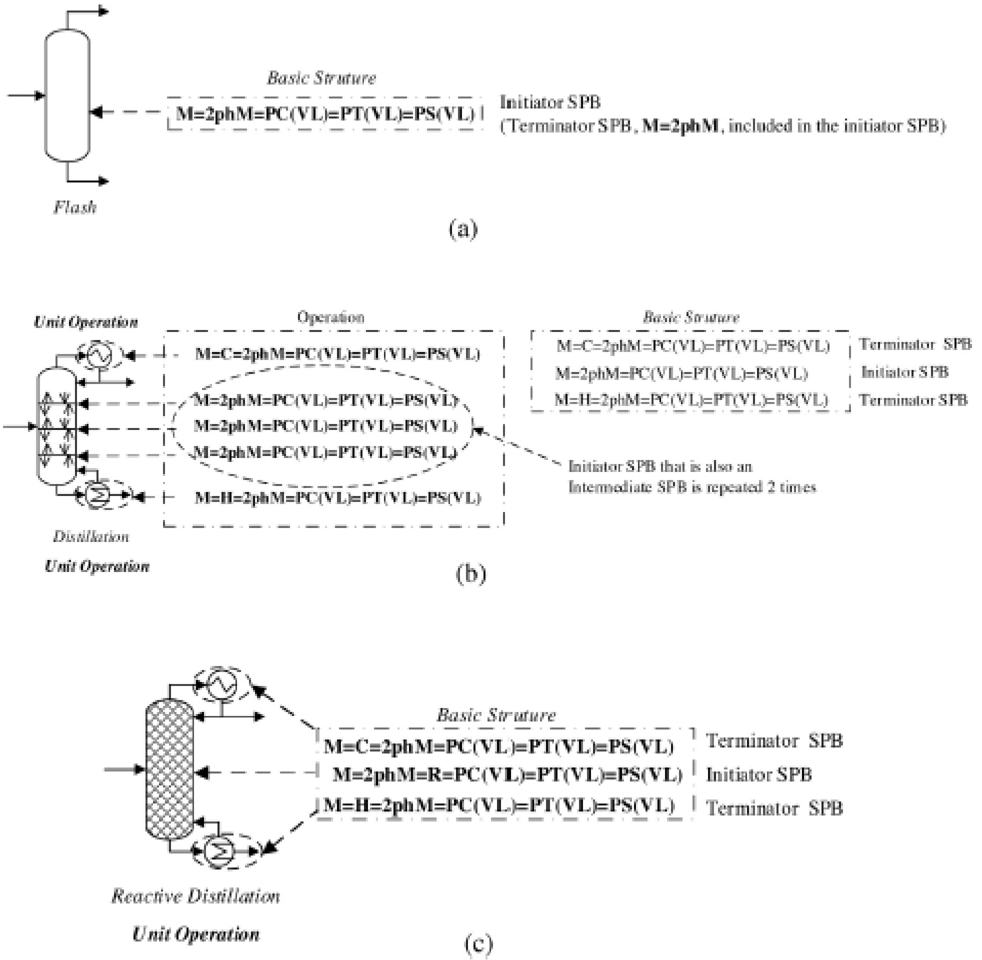


Figure 3.5 – The generation of feasible SPBs that represents process alternatives. a) flash vessel, b) distillation column and c) reactive distillation column.

C.2. - Basic structures

A basic structure is defined as the combination of multiple SPBs using predefined combination rules (Babi *et al.*, 2014). A basic structure performs a targeted or set of targeted tasks and is represented by SPBs, which are classified as initiator, intermediate and terminator. An initiator SPB is one that fulfills the main objective of a task but may not fulfill the entire task. A terminator SPB represents the final task to be performed in an operation. An initiator SPB, when repeated more than once to represent an operation is classified as an intermediate SPB. These intermediate SPBs can be repeated multiple times to complete the tasks of an operation. A basic structure can then be expanded in order to fulfill a task. When a basic structure is expanded and fulfills a task, it is referred to as the completion of the desired (needed) operation which is then translated into a unit operation (see Figure 3.4). The number of times intermediate SPBs can be repeated is determined by using the extended Kremser method (Lutze *et al*., 2013), for example, the number of trays of a distillation column is equivalent to the number of repeated intermediate SPBs. For a flash vessel the basic structure is also an operation and as it performs (see Figure 3.4(a)) the desired separation task. However, for the distillation column and reactive distillation column, intermediate SPBs must be added until the process specifications (such as product purity, recovery, etc.) are matched (see Figure 3.4(a)–(c)).

3.4 Sustainability metrics and performance criteria

In this methodology the sustainability metrics defined by the Institution of Chemical Engineers by Azapagic (2002) have been used. The author has defined 49 metrics divided into three main areas: environmental, social and economic. The use of the sustainability metrics follows the simple rule that the lower the value of the metric the more effective the process. A lower value of the metric indicates that either the impact of the process is less or the output of the process is more. For the environmental impact related metrics (see Fig. 5), instead of using the definition of Azapagic (2002); the definition proposed by Cabezas et al. (1999) have been used and proposed the WAR algorithm in order to calculate the environmental impacts from a chemical process.

This algorithm has been implemented as part of the indicator-based methodology. To calculate these metrics, the flowrates for each compound coming into the process and leaving the process are needed as known information. Summarizing, the indicators are applied to the entire set of open- and closed-paths. With their values the critical points of the process as well as the areas that should be improved in the process are determined. The sustainability metrics and the safety index are calculated using the steady-state data for the global process and they are used to measure the impact of the process in its surroundings. They will be used as performance criteria in the evaluation of the new suggested design alternatives.

In order to evaluate a more sustainable design compared to the base case design for identifying non-tradeoff designs, different performance criteria related to economic, sustainability/LCA factors are applied (Eq. (3.28)).

These are categorized as follows:

3.4.1. Sustainability metrics/LCA factors – Environmental related

a. Sustainability metrics, Carbon footprint:

The sustainability metrics are presented in the three groups

- Environmental indicators
- Economic indicators
- Social indicators

Which reflect the three components of sustainable development. Not all the metrics we suggest will be applicable to every operating unit. For some units other metrics will be more relevant and respondents should be prepared to devise and report their own tailored metrics. Choosing relevant metrics is a task for the respondent. Nevertheless, to give a balanced view of sustainability performance, there must be key indicators in each of the three areas (environmental, economic and social). Most products with which the process industries are concerned will pass through many hands in the chain resource extraction – transport – manufacture – distribution – sale – utilization – disposal – recycling – final disposal. Suppliers, customers and contractors all contribute to this chain, so in reporting the metrics it is important that the respondent makes it clear where the boundaries have been drawn. As with all benchmarking exercises, a company will receive most benefit from these data if they are collected for a number of operating units, over a number of years, on a consistent basis. This will give an indication of trends, and the effect of implementing policies (Azapagic, 2002).

b. Environmental impacts:

For the life cycle assessment, the benefit of this analysis is to compare the process alternatives in term of environmental impacts. The uses of carbon footprint are also integrated to this analysis to achieve the more sustainable design. The systematically framework for calculating the important LCA factors are represented in Figure 3.6.

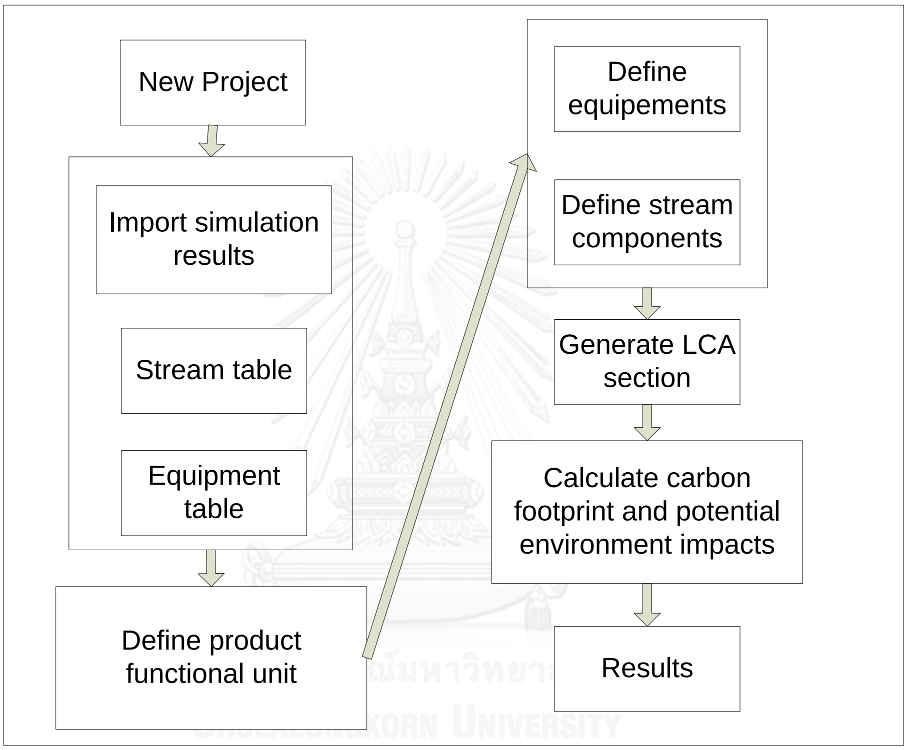


Figure 3.6 - Work-Flow in environmental impact assessment.

As input data, the software needs a detailed mass balance of the production process and the duties of all equipment in the process. Additionally, a careful analysis of the system boundaries must be performed because one needs to specify the origin of each compound present in the system. In other words, one needs to know the origin of every compound that is shown in the mass balance, whether it is a product, by-product, chemical, or raw material.

Moreover, Table 3.3 lists the 11 PEIs calculated by LCSoft, together with a brief description of each one which these impacts will be using as the process performance criteria.

Table 3.3 - Brief Description of the PEIs.

Environmental Metrics	
HTPI (1/LD 50)	Human toxicity from ingestion and inhalation is used as a measure to estimate the toxicity potential because they take into account the primary routes of exposition to a chemical. The compound is analyzed at 0 °C and normal pressure. The concentration that caused death in 50% of a test population of rats by oral ingestion was used as HTPI estimate. Molecular methods were used in certain cases when LD50 data were not available.
HTPE (1/TWA)	Human toxicity from dermal exposure, similar to HTPI in terms of significance. To estimate HTPE, time-weighted averages of the threshold limit values (TLV) were used, obtained from OSHA, ACGIH, NIOSH, and represent occupational safety exposure limits. Those values are currently being used as measurement values in LCSoft database.
GWP (CO_2 eq.)	Global warming potential is determined by comparing the extent to which a compound absorbs infra-radiation over its atmospheric lifetime and the extent that CO_2 absorbs infrared radiation over its respective lifetimes. The compounds half-life time was also considered for this measure calculation; 100 years was the base timeframe chosen by LCSoft.
ODP (CFC-11eq.)	Ozone depletion potential is estimated by comparison the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen. For a compound is considered to have

	impact on this field, it must contain chlorine or bromine and remain in the atmosphere long enough to reach the stratosphere.
PCOP (C_2H_2 eq.)	Photochemical oxidation or smog formation potential is estimated by comparison of the rate at which a unit of mass reacts with a hydroxyl radical with the rate at which a unit mass of ethylene reacts with the same radical.
AP (H_1 eq.)	Acidification potential or acid rain potential is calculated by comparing the rate of release of H_1 to the atmosphere as promoted by a chemical to the rate of release of H1 into the atmosphere as promoted by SO_2.
ATP (1/LC 50)	Aquatic toxic potential is estimated based on the concentration of a compound in freshwater that causes death in 50% of the animal population being tested.
TTP (1/LD 50)	Terrestrial toxic potential is estimated based on the concentration of a compound in land sites that causes death of 50% of the animal population being tested.
HTC (kg of benzene eq.)	Human toxicity carcinogens include chemical emissions to urban air, rural air, agricultural soil, and natural soil.
HTNC (kg toluene eq.)	Human toxicity non-carcinogenic impacts include chemical emissions to urban air, rural air, agricultural soil, and natural soil.
ET (kg 2,4-Dichlorophenoxyacetic acid eq)	Eco-toxicological toxicity includes impacts for emissions to urban air, rural air, freshwater, and agricultural soil.

3.4.2. Economic – Cost related

- Economic analysis

One of the major process performance criteria, for selecting the best process alternative, the economic analysis is one of the important issues to consider. The equipment cost calculation, capital investment cost calculation, operating cost calculation, PIE chart analysis, sensitivity analysis, and alternative comparison are need to analysis. The work flow for economic analysis is represented in Figure 3.7 which required the raw material cost, utilities cost such as high pressure steam ($/MJ), sizing and type of process equipments.

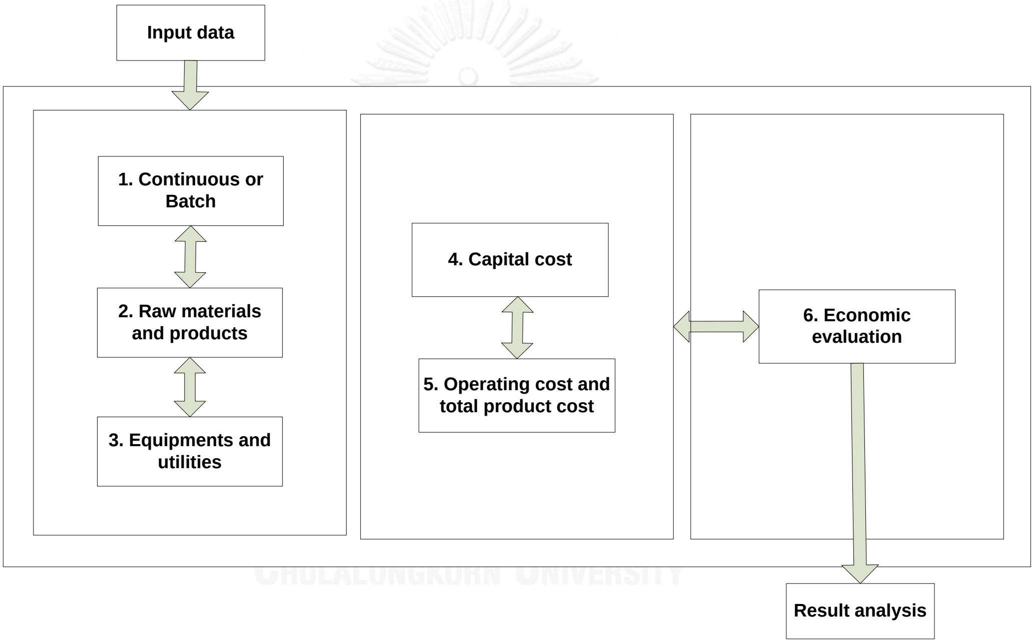


Figure 3.7 - Work-Flow for economic analysis.

CHAPTER IV

PROPOSED METHODOLOGY FOR SUSTAINABLE PROCESS DESIGN

Process design is performed when developing new technologies, when creating new facilities, or when retrofitting existing production processes. From data gathering and process flow sheet synthesis to detailed design and optimization steps, the traditional approach in process design considers only the economic and technical aspects as the main criteria. With increasing demands for sustainable growth, more performance measures have been proposed and incorporated into process design to achieve the sustainability goal. In this section, the framework for sustainable process synthesis and design is presented together with its implemented computer-aided methods and tools. The framework allows the designer to assess the sustainability potential of a specified production process and provides computer-aided methods and tools to generate and compare more sustainable processing alternatives that match the process product specifications. A number of metrics (techno-economic, LCA, safety, etc.) have been used for assessing the level of sustainability and for identifying more sustainable options. The design methodology comprises a sequence of steps with various computer-aided tools that are used to perform calculations of the metrics (also known as sustainability indicators) systematically and efficiently. The framework enables the designer to link between sustainability potential, process de-bottlenecking, improvements, and possible trade-offs. Raw material, water, and energy usage, as well as LCA and economic impact, are some of the metrics that are used for multi-criteria evaluation of generated design alternatives.

The proposed framework includes methods and tools for identification of critical points (bottlenecks) within the process. Another set of computer-aided methods and tools is used for the generation of retrofit (or new) design options through a heuristic strategy. The next stage comprises testing and screening of the generated options in terms of feasibility (matching of process specification) and sustainability (matching of improvement targets). That is, the best options to overcome the identified critical points matching the design targets are evaluated in detail in terms of environmental feasibility, sustainability, and economic profitability. Therefore, this framework should be able to serve as a decision-making tool that allows the assessment of the production plant performance with respect to the objectives embedded in the idea of sustainable development and as a means for screening among feasible process options for the production of the desired product. As shown in Figure 4.1, the overview of the framework proposed by Babi *et al*., (2015) consists of three-stages involving a synthesis-stage, a design-stage and an innovation-stage that are briefly discussed below.

Stage-I: Synthesis-stage

The objective here is to quickly find an optimal processing network or a small set of most promising networks for converting a given set of raw materials to a desired set of products. Data on known technologies are used to generate a superstructure of alternatives, based on an integrated business and engineering framework for synthesis and design of processing networks (Zondervan *et al*., 2011; Quaglia *et al*., 2013). Different mathematical programming problems are formulated and solved, employing factors such as product yield, minimization of waste, operating-material costs, etc., as performance criteria. The result from this stage is an optimal processing route or a set of promising processing routes for converting the given raw materials to the desired products using known technologies for each processing step.

Stage-II: Design-stage

The objective here is to establish a base case design by selecting one or more promising process routes from stage-1 in terms of a selected set of performance criteria (energy consumption, net CO_2 emission, raw material depletion and life cycle assessment factors); to perform economic analysis, life cycle assessment analysis and sustainability analysis on the base case design to identify process “hot-spots” (process limitations or bottlenecks); to define targets for process improvements through the minimization and/or elimination of the process “hot-spots”. A rigorous simulation is performed in this stage to generate the necessary data.

Stage-III: Innovation-stage

The objective here is to generate and evaluate process alternatives that match the established targets for process improvements. The phenomena-based process intensification method (Lutze *et al*., 2013; Babi *et al*., 2015) is employed here. Process alternatives that match the targets are better, by definition, than the base case design and are also more sustainable. In the final step, a rigorous simulation is performed to verify all aspects of the selected more sustainable process alternative.

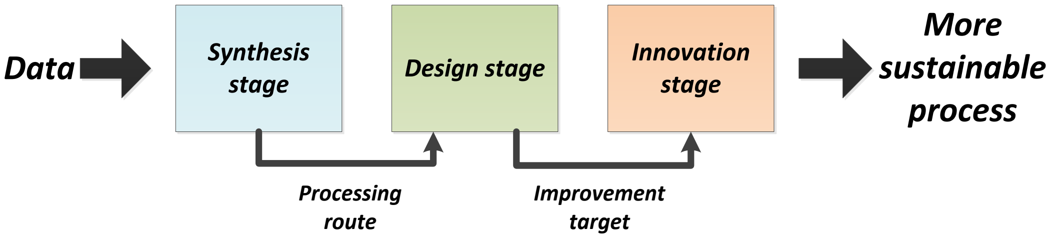


Figure 4.1 - The overall framework for synthesis-design-innovation of more sustainable process designs as inspiration from the work by Babi *et al*., 2015.

The work-flow of the combined synthesis-design-intensification framework is highlighted in Figure 4.2. A step-by-step description of the work-flow is given below.

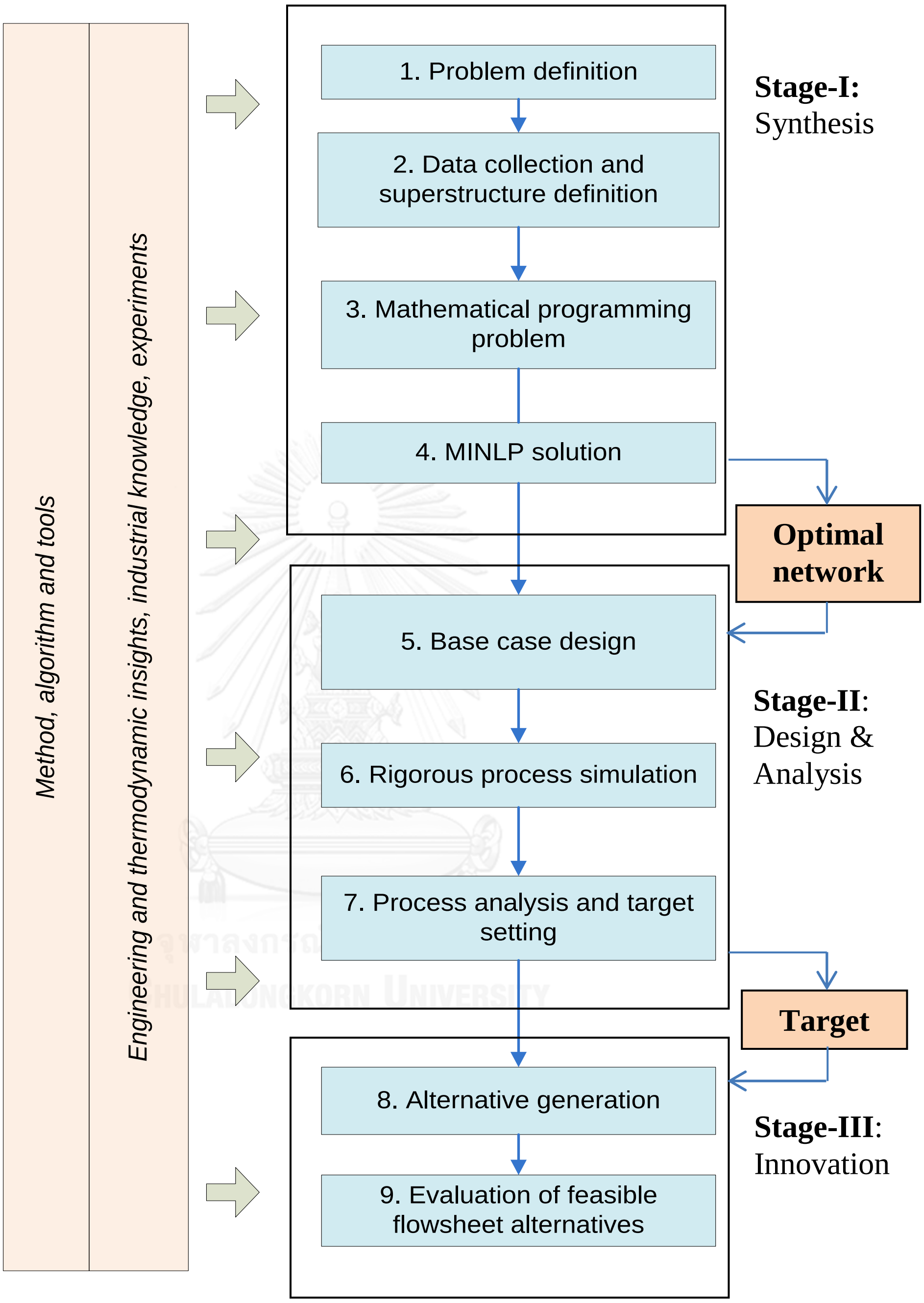


Figure 4.2 - Framework for more sustainable process synthesis and design.

Step 1. Problem definition

The objective of this step is to define the problem that needs to be investigated and solved. The products to be produced, the raw materials (feed-stocks) to be converted, the performance criteria to be used, etc., are defined here. Based on these, the appropriate data need to be collected. The problem definition step is broken-down into the following 2 sub-steps:

Step 1.1: Data requirement: the main products and by products, the feed-stock to be used and the list of known technologies to connect the raw material to the desired products are specified here.

Step 1.2: Selection of the objective function, the performance criteria and process constraints are made here.

Step 2. Data collection and superstructure definition

The objective of this step is to collect the data needed to define and solve the more sustainable process synthesis-design problem. The network superstructure consists of processing steps and under each processing step, known process technologies are arranged as intervals. In a process interval, operations such as reaction, separation, mixing, etc., can take place. The concept of a network (superstructure) of processing routes in term of processing steps and intervals is illustrated in Figure 4.3.

Based on the known technologies for the conversion of the selected feed-stocks to the desired products, a superstructure of processing networks is developed. Figure 4.4 shows the process interval model where operational-processing tasks, such as mixing, reaction, separation, transportation, or their combination may take place. The important data for each of the process intervals are collected and organized in a predefined knowledge structure (Quaglia *et al*., 2013) in this step.

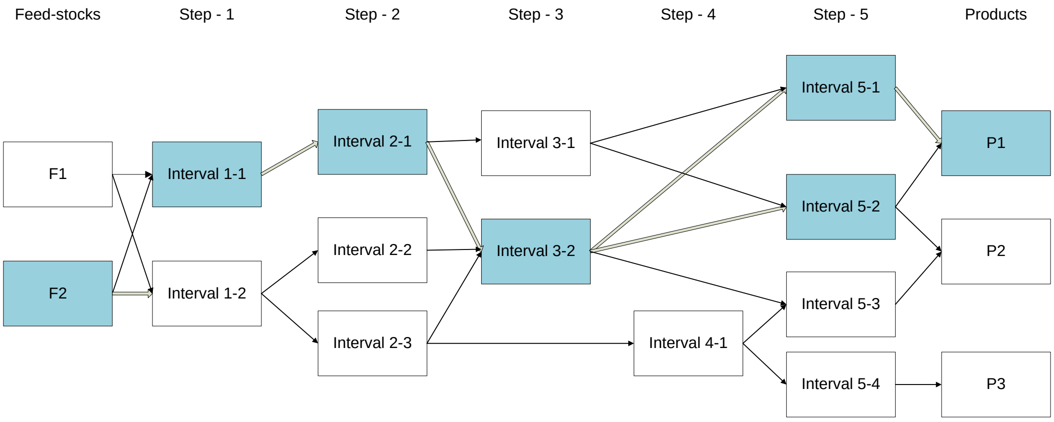


Figure 4.3 - The generic form of superstructure and GAMS user interface for superstructure generation (the blue boxes indicate a likely processing route the optimal network is indicated).

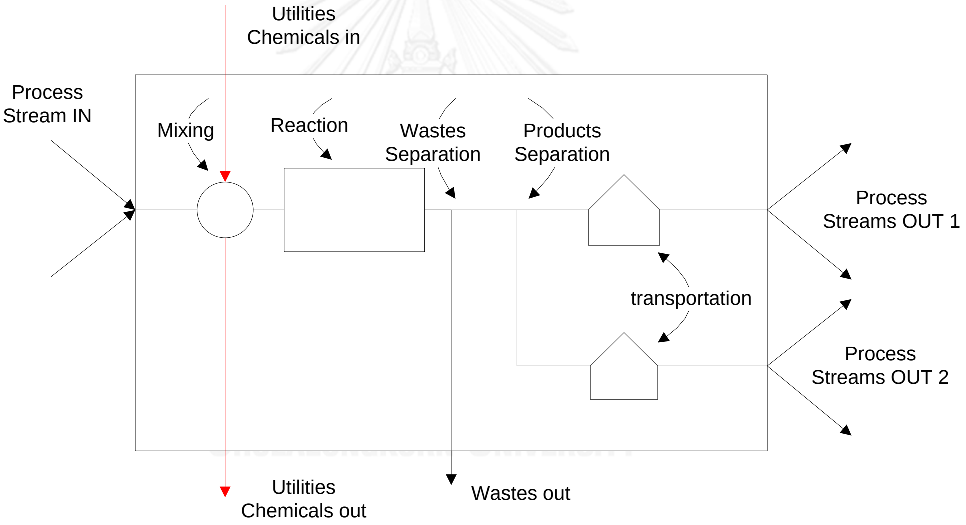


Figure 4.4 - Generic model of a process interval (proposed by Quaglia *et al*., 2013).

Step 3. Mathematical programming problem

This step is divided into two sub-steps:

Step 3.1: Model generation –The objective of this step is to select the mathematical models for each interval so that a total mathematical model of the superstructure can be developed and validated. For each processing step and the corresponding interval description, the appropriate models are retrieved and the consistency of the model-data is checked (that is, the collected data should include all the model parameter values). A check of consistency of available data and the generated model is also performed in this step. At the end of this step, all the model equations representing the superstructure are obtained.

Step 3.2: Here, the mathematical programming problem is formulated, based on the problem definition of step 1, the collected data of step 2 and the mathematical model from step 3.1. The objective function maybe given as indicated in Eq. (4.1). The superstructure, the interval models, the logical constraints and the variable bounds defined in step-2 constitute an MILP or MINLP model (Eqs. (4.1)–(4.6)) (Zondervan *et al.*, 2011; Quaglia *et al.*, 2012, 2013).

$$\max f(x, y) \tag{4.1}$$

Subject to:

$$g(x, y) \geq 0 \tag{4.2}$$

$$h(x, y) = 0 \tag{4.3}$$

$$x \in X; \tag{4.4}$$

$$x^{LO} \leq x \leq x^{UP} \tag{4.5}$$

$$y \in \{0; 1\}^n \tag{4.6}$$

Where f is the objective function, x represents the vector of continuous variables defined by their upper and lower bounds x^{UP} and x^{LO} in a continuous feasible region X; y is the vector of binary variables where intervals may or may not be connected at a processing step, g and h represent inequality and equality constraints, respectively. The process model consisting of component mass balance and energy balance equations are represented by Eq. (4.7).

$$F(\gamma_{i,kk,rr}\,,\ \theta_{react,kk,rr}\,, \alpha_{i,kk}, Mw, SW_{i,kk}, S_{i,kk}, \xi^{P}_{k,kk}) = 0 \tag{4.7}$$

An example of Eq. (4.1) is given by Eq. (4.8).

$$\boldsymbol{Max\,Profit} = \textstyle\sum_{i,kk}\left(P3_{i,kk} \cdot F^{out}_{i,kk}\right) - \sum_{i,kk}\left(P2_{i,kk} \cdot R_{i,kk}\right) - \sum_{i,kk}\left(P1_{i,kk} \cdot F^{out}_{i,kk}\right) - W^{Price} \cdot \sum_{i,kk}\left(F^{R}_{i,kk} \cdot SW_{i,kk}\right) - \frac{CAPEX}{\#year} \tag{4.8}$$

where γ represents the stoichiometric, θ is the fraction of converted reactant, α is the quantity of chemical consumed, MW_i contains the molecular weight of the components, SW contains the produced quantities of waste, S_i are the split factors of the components entering and interval and ξ is a matrix to match interval k and kk. Based on the information collected, the superstructure is created together with the list of decision variables that will need to be determined. The process model equations (Eq. (4.7)) are obtained from the generic interval model (Quaglia *et al.*, 2013). Special software (Quaglia *et al*., 2013) is employed to create the superstructure network and the corresponding mathematical programming problem to be solved by GAMS (IBM Corp, 2009).

Step 4. MILP/MINLP solution

Here, the MILP/MINLP problem formulated in step 3 is solved with GAMS (IBM Corp, 2009). Different objective functions may be defined to obtain different processing paths. The selection of the interval model equation options decides if the problem is MILP or MINLP.

Step 5. Base case design

The objective here is to add details to the optimal processing route from step 4 to obtain a base case design in terms of equipment (design) parameters. For example, for a distillation column, the number of stages, the feed location, product recovery rates, etc., are fixed at this stage so that a rigorous simulation of the base case can be performed.

Step 6. Rigorous process simulation

The objective here is to perform a rigorous process simulation of the base case design. In principle, any process simulator could be used. However, before a rigorous simulation can be performed, it is important to check if all the necessary data are available. The appropriate unit operation models together with the consistent thermodynamic models will need to be employed from the selected simulator.

Step 7. Process analysis and target setting

The objective of this step is to perform analyses of the base case design in terms of sustainability, including LCA factors and economics so that process deficiencies (regarded as process “hot-spots”) can be identified and targets for overcoming these “hot-spots” are defined. Here, the sustainable design method of Carvalho *et al*., (2013) is employed.

Step 8. Alternative generation

The objective of this step is to find alternatives that match the design targets and thereby lead to a more sustainable design. The design targets are specified in terms of process efficiency, productivity and sustainability as well as reduced energy consumption, waste generation, and environmental impact. More details of the process intensification based method employed here can be found in Babi *et al*., (2014). The method operates at the phenomena level and the concept is similar to that of computer-aided molecular design (CAMD) where groups of atoms are used as building blocks to generate new as well as known molecules with desired (target) properties. Using this method, a systematic identification of necessary and desirable (integrated) phenomena as well as generation and screening of phenomena-based flowsheet options are made using a decomposition-based solution approach.

Like the CAMD technique, the phenomena based synthesis (PBS) method also operates at different levels of aggregation where the flowsheet decomposed in terms of unit operations, which are represented by a set of tasks (Siirola *et al*., 1971; Siirola, 1996) for which, all the selected phenomena are identified by combining the phenomena in different ways, the same tasks can be performed, thereby leading to new and more sustainable alternatives that match the design targets. The concept of phenomena based synthesis is illustrated through Figure 4.5, where it can be noted that starting with a base case flowsheet, a set of phenomena found in it are identified, which are then combined to form multiple flowsheets that are likely better than the base case.

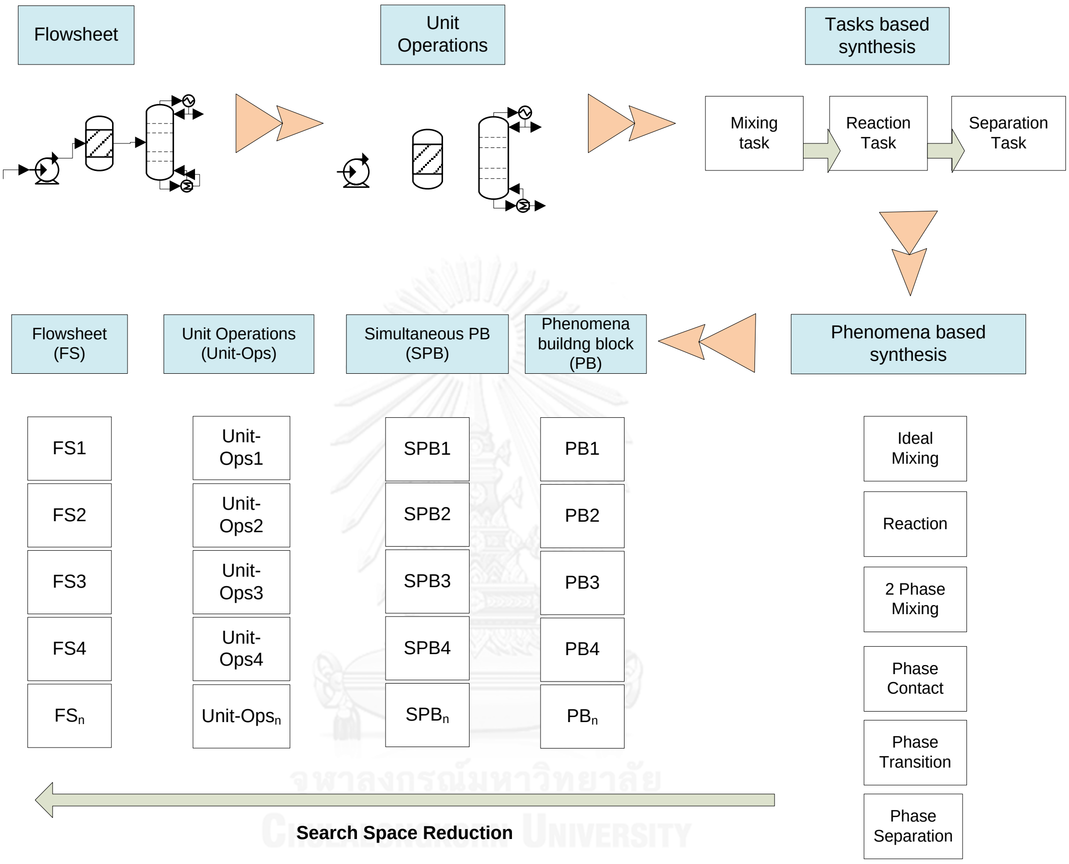


Figure 4.5 - Illustration of Phenomena based synthesis of process alternatives (adapted from Babi, Woodley, & Gani, 2014).

The phenomena currently considered are classified as: 1) mixing-M (mass flow within one or several phases), 2) phase contact-PC (the contact and resistances at phase boundaries of phases), 3) phase transition-PT (mass transfer of compounds between two phases), 4) phase change-2phM (state change of a complete stream at no phase transition), 5) phase separation-PS (the degree of separation of two phases), 6) reaction-R (change in mass of a compound or compounds generated or consumed between inlet and outlet), 7) energy transfer-H/C (energy transfer between sources and sinks of energy) and 8) stream dividing-D (division of a stream into two or more streams).

Step 9. Process evaluation

After the process alternatives are generated in step 8, they are further analyzed in terms of economic and LCA evaluations. The objective of this step is to evaluate the alternatives to identify the best (or a sub-set) process. The performance evaluation of process alternatives are established in terms of carbon footprint (CF), which is the overall amount of carbon dioxide and other greenhouse gas emissions associated with one kilogram of product. The carbon footprint is related to other indicators such as the global warming potential (GWP) in terms of kg of CO_2 equivalent. For the health issues, an indicator such as the human toxicity-carcinogenic (HTC) is used in terms of kg of benzene equivalent. Economic evaluation is calculated using ECON (Saengwirun, 2011) which provides the needed cost and economic potential data.

CHAPTER V

PRELIMINARY EVALUATION OF DIFFERENT CO_2-BASED PROCESS FOR DIMETHYL CARBONATE PRODUCTION

The production of DMC is classified here in terms of two main types, namely conventional processes and CO_2-based processes. Among the conventional processes, the productions of DMC from phosgene, through partial carbonylation of methanol (BAYER process) and from methyl nitrile (UBE process) are well-known. The processes utilizing CO_2 include direct synthesis with methanol and integrated processes involving intermediate compounds such as urea, propylene carbonate and ethylene carbonate, which are derived from CO_2. The involved reactions and associated thermodynamic data are given in Table 5.1 for the above process routes.

5.1 Conventional process

5.1.1 Synthesis of DMC from Phosgene

This process employs the traditional (pre-1980) method to produce DMC (Pacheco *et al.*, 1997). Here, phosgene reacts with methanol to form methyl chloroformate (CH_3OCOCl), which further reacts with methanol to form DMC according to Eq. 5.1 in Table 5.1. However, phosgene is an extremely hazardous material (Matsuzaki *et al.*, 1997) and is classified by the US Department of Transportation (DOT) as a class-A poison. Consequently, there is an incentive to phase out phosgene (Matsuzaki *et al.*, 1997).

5.1.2 DMC from Partial Carbonylation (BAYER process)

This non-phosgene process produces DMC by reacting methanol, carbon monoxide and oxygen in liquid phase, as given by Eq. 5.2 in Table 5.1. As the catalyst, Cu(I)Cl and KCl in various ratios are usually employed (Kricsfalussy *et al.*, 1996; Tundo *et al.*, 2002). The process however suffers from low production rate, difficulties in downstream separation because of the existence of binary azeotropes in the system methanol-water-DMC, and the need for corrosion resistant reactors. Nevertheless, the process has been licensed by BAYER for commercial production of DMC.

5.1.3 DMC from Methyl nitrite process

The oxidative reactions using the alkyl nitrites as an oxidant have been developed by UBE (Matsuzaki *et al.*, 1997, Tundo *et al.*, 2002). In the alkyl nitrite reactions, substrates such as CO and carbonyl-compounds are oxidized over palladium catalysts. The DMC, dialkyl oxalates and other useful chemicals are synthesized efficiently under moderate conditions by this type of alkyl nitrite reactions. In the case of DMC, methyl nitrile reacts with carbon monoxide to produce DMC and nitric oxide, as given by Eq. 5.3 in Table 5.1. This processing route has difficulties due to the production of nitric oxide, which is toxic and therefore, its release must be controlled and regulated. However, it is noteworthy that this methyl nitrile process has been employed for further production of dimethyl oxalate (Matsuzaki *et al.*, 1997).

5.2 CO_2 as chemical feedstock for DMC production

Production of DMC from CO_2 is feasible through direct reaction with methanol or via the formation of intermediate compounds such as urea, propylene carbonate or ethylene carbonate. The latter is highlighted in Figure 5.1. In this work, it is assumed that a pure CO_2 feed stream, captured through a process is available, irrespective of the emission source. Some of the sources of CO_2 emitted streams could be, natural gas sweetening process, ammonia process, ethylene oxide process, H_2 production process and fermentation process. The CO_2 from higher concentration sources has the advantage that they may be directly applicable in the considered reaction scheme, thereby avoiding additional purifying steps. On the other hand, high purity CO_2 streams would avoid catalyst deactivation, avoid side reaction from impurities and lead to low energy consumption in utilities and separation sections. It should be noted that the savings being considered here is not in the effort to capture and purify but in the potential effort to sequestrate. In this way, the capture effort is the same and must be done but the sequestration effort is reduced by diverting some of the CO_2 for utilization efforts.

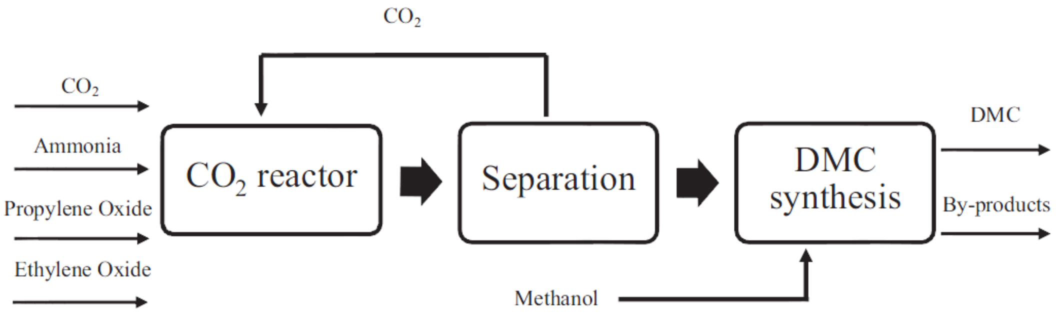


Figure 5.1 - Concept of CO_2-based processes for production of dimethyl carbonate by CO_2 conversion.

5.2.1 DMC from direct synthesis from CO_2 and methanol

For the direct use of CO_2 to produce DMC, it has been reported that CO_2 could react with methanol at critical temperature and critical pressure of CO_2 as highlighted by Eq. 5.4 in Table 5.1 (Wu *et al*., 2006; Gu *et al*., 2008; Fang *et al*., 1996). Under mild conditions, a basic catalyst (ZrO_2-MgO), a promoter (methyl iodide) and butylene oxide as a chemical trap to shift the chemical equilibrium are needed (Eta *et al*., 2011).

This direct reaction route results in high atom-efficiency and avoids the use of toxic chemicals such as phosgene. However, industrial utilization of CO_2 in the direct DMC synthesis is still a significant challenge because CO_2 lies in a deep potential energy well of about −400 kJ/mol that requires a huge amount of energy for activation (Eta *et al*., 2011).

5.2.2 DMC synthesis from urea (urea-route)

DMC can also be synthesized from CO_2 via urea (Sun *et al*., 2005). This process, proposed as a new alternative, integrates the synthesis of urea and DMC, where CO_2 is used as a chemical feedstock. The process starts with the reaction between CO_2 and ammonia in the urea synthesizer, which is operated at 165-190 ˚C and 135-205 bar (Sheppard *et al*., 2003). The product stream is pumped to the purification section to remove water, excess CO_2 and ammonia from urea. Then, methanol is added for the alcoholysis reaction to produce DMC by using ionic liquid

Et_3NHCl–$ZnCl_2$ or emimBr–$ZnCl_2$ (Wang *et al.*, 2009). It has been reported that the process involves a two-step reaction with methyl carbamate as the reaction intermediate as given by Eqs. 5.5-5.7 in Table 5.1 (Wang *et al.*, 2009).

5.2.3 DMC synthesis from propylene carbonate (PC-route)

One of the most promising ways to effectively utilize CO_2 in DMC production is through cycloaddition of CO_2 to epoxides to form cyclic carbonates (Watile *et al.*, 2012), which gives 100% atom efficiency. Propylene carbonate (PC) is synthesized from propylene oxide (PO) and CO_2 at 130 ˚C and 20 bar (see Eq. 5.8 in Table 5.1). Subsequently, DMC is obtained through the transesterification of propylene carbonate and methanol (see Eq. 5.9 in Table 5.1). Various type of catalysts can be used, such as, basic quaternary ammonium ion exchange resins with hydroxide counter ions. Also, Verkade super bases can be effective at low catalyst loadings for the rapid transesterification of propylene carbonate with methanol under mild conditions and with high product selectivity (Williams *et al.*, 2009; Li *et al.*, 2006). For this reaction, propylene glycol which is a valuable chemical is obtained as a by-product.

5.2.4 DMC synthesis from ethylene carbonate (EC-route)

Similar to the synthesis of propylene carbonate, ethylene carbonate (EC) is also produced from cycloaddition of CO_2 to ethylene oxide (EO) (see Eq. 5.10 in Table 5.1). The reaction condition is relatively mild, i.e., 30 ˚C and 25 bar in immobilized ionic liquid on amorphous silica (Kim *et al.*, 2010). Subsequent transesterification of ethylene carbonate with methanol produces DMC and ethylene glycol (see Eq. 5.11 in Table 5.1). It has been reported that the conversion of ethylene carbonate to DMC is 81.2% at 250 ˚C and 90 bar. Various type of catalysts can be used, such as poly-4-vinyl pyridine as a novel base catalyst and DABCO-derived (1,4-diazobicyclo[2.2.2]octane) basic ionic liquids (Jagtap *et al.*, 2008; Yang *et al.*, 2010).

Table 5.1 - List of selected reactions found in DMC production

Process	**Reaction**		**$\Delta G_{r25^{\circ}C}$ (kJ/mol)**	**$\Delta H_{r25^{\circ}C}$ (kJ/mol)**
Phosgene route	$COCl + 2CH_3OH \rightleftharpoons (CHO)CO + 2HCl$	(5.1)	-305.543	-321.670
Partial carbonylation	$CO + 1/2O_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$	(5.2)	-233.077	-300.399
Methyl nitrile	$CO + 2CH_3ONO \rightleftharpoons (CH_3O)_2CO + 2NO$	(5.3)	-115.438	-107.945
CO_2 direct synthesis	$CO_2 + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + H_2O$	(5.4)	29.583	-15.259
Urea route	$2NH_3 + CO_2 \rightleftharpoons NH_2CONH_2 + H_2O$	(5.5)	21.009	-0.042
	$NH_2CONH_2 + CH_3OH \rightleftharpoons CH_3OCONH_2 + NH_3$	(5.6)	-13.240	-10.310
	$CH_3OCONH_2 + CH_3OH \rightleftharpoons (CH_3O)_2CO + NH_3$	(5.7)	15.390	13.11
Propylene carbonate route	$C_3H_6O + CO_2 \rightleftharpoons CH_3(C_2H_3O_2)CO$	(5.8)	-0.054	-0.908
	$CH_3(C_2H_3O_2)CO + 2\ CH_3OH \rightleftharpoons (CH_3O)_2CO + C_3H_8O_2$	(5.9)	35.115	22.854
Ethylene carbonate route	$C_2H_4O + CO_2 \rightleftharpoons (CH_2O)_2CO$	(5.10)	-0.025	-0.083
	$(CH_2O)_2CO + 2CH_3OH \rightleftharpoons (CH_3O)_2CO + (CH_2OH)_2$	(5.11)	-14.926	27.500

5.3 Screening of Process Routes

The objective of this analysis is to preselect three of the most promising process alternatives as candidates for further analysis based on the thermodynamic feasibility of their synthesis routes together with environmental, safety and health concerns.

5.3.1 Thermodynamic analysis

The reaction equilibrium for different reactions is calculated using Aspen Plus® software where all necessary model parameters are available. The feasibility of reactions is verified through the equilibrium reactor model in Aspen Plus®, which is based on Gibbs free energy minimization. The liquid activity calculation, the UNIQUAC model (Zhang *et al*., 2005; Holtbruegge *et al*., 2013) has been used and these values were cross-checked with the NRTL (Nikoo *et al*., 2011) and PSRK (Nikoo *et al*., 2013; Smith *et al*., 2005) models. In Table 4.1 the calculated values of Gibbs free energy, the heat of reaction and the equilibrium constant at 25 ˚C are listed for all the reactions involved, while in Figure 5.2, calculated values of the Gibbs free energy as a function of temperature and at standard pressure of 1 bar are highlighted. Based on these results, the CO_2 direct synthesis route is eliminated because of the positive Gibbs energy values, while the phosgene route and the methyl nitrile route are eliminated because of environmental, safety and health issues, even though the involved reactions have very favorable Gibbs free energy values. Their designs and performance are also well documented.

Considering the CO_2-based processes, the urea-route, EC-route and PC-route are considered as at higher pressures they are thermodynamically favorable. At the temperature of the reaction of urea synthesis (reaction 5), the Gibbs energy is positive, as given in Table 5.1 and shown in Figure 5.2. However, the Gibbs free energy for reaction 5.5 has been found to be negative at 160 bar and 200˚C, while the Gibbs free energy of CO_2 to urea synthesis is -70 kJ/mol, even though at 1 bar and 25 ˚C it is 21 kJ/mol (Zhang *et al*., 2005). The CO_2 coupling reactions to propylene carbonate (reaction 8) and ethylene carbonate (reaction 10) show slightly negative values of Gibbs free energy at lower temperatures, indicating that these two reactions are feasible for CO_2 utilization. This leaves for further analysis, the partial carbonylation route (BAYER process), the CO_2-based urea-route, EC-route and PC-route.

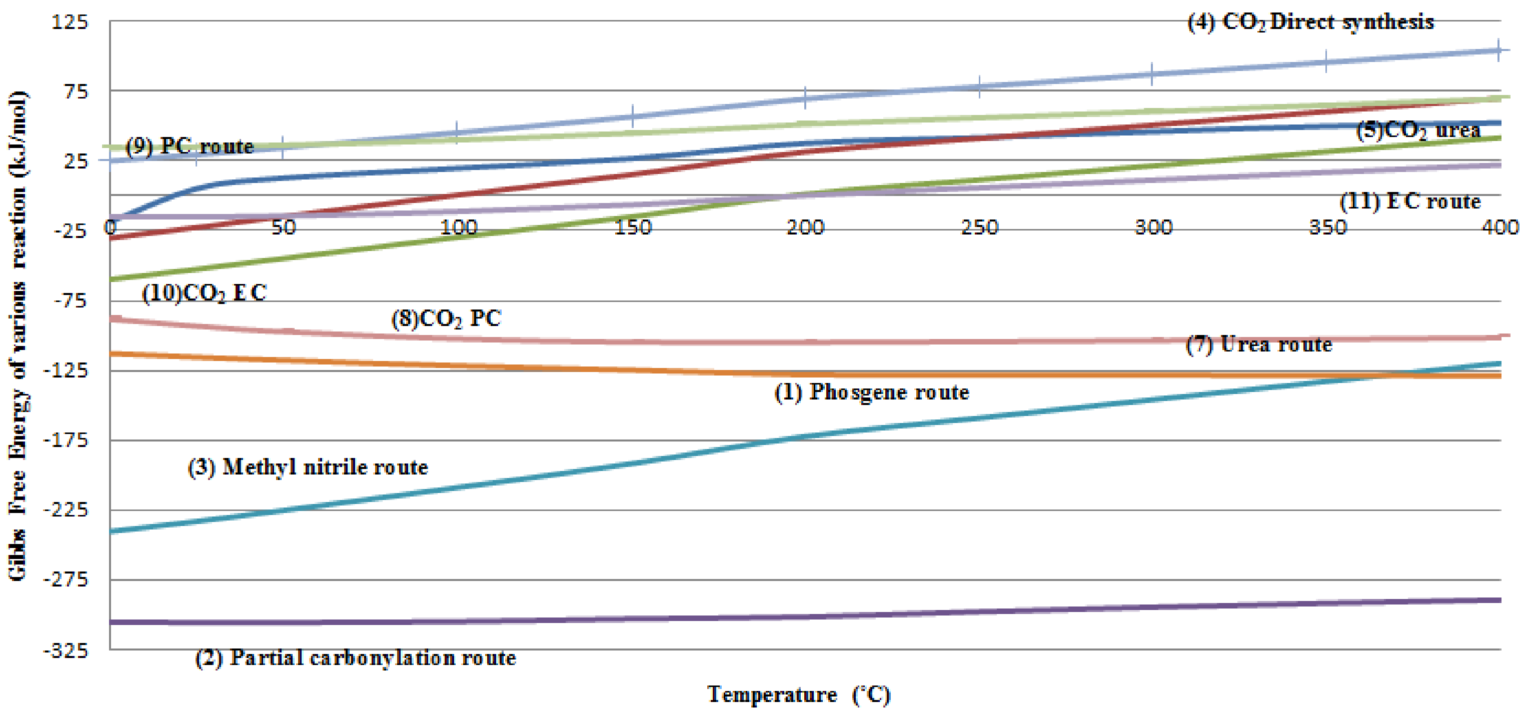


Figure 5.2 - Gibbs free energy for different reactions involving DMC production: phosgene route (1), partial carbonylation route (2), methyl nitrile route (3), direct CO_2 synthesis route (4), urea route (7), propylene carbonate route (9) and ethylene carbonate route (11) and CO_2 coupling reaction to urea (5), propylene carbonate (8), and ethylene carbonate (10)

5.3.2 Sensitivity analysis

A sensitivity analysis is now performed for the three CO_2-based DMC production routes to identify the reactor operating windows for these processes in terms of product (DMC) yield, temperature and pressure. The simulations are based on the equilibrium reactor model in Aspen Plus® and the calculated values are validated-compared with known experimental values. In these simulations, the feed compositions of Urea-MeOH, EC-MeOH and PC-MeOH are kept constant at their stoichiometric ratios (1:2 for all reactions), while pressure (P) and temperature (T) are varied. The operating conditions for these synthesis routes are known to vary as follows:

- Urea route: 4-12 bar for pressure; 125 ˚C to 250 ˚C for temperature. A yield of 67.4% is reported for the reaction between urea and methanol using polyphosphoric acid as a catalyst at 8 bar and 150 ˚C (Wang *et al.*, 2009).
- EC route: 1-15 bar for pressure; 25 ˚C to 250˚C for temperature. The yield is reported to be 75.3% for the reaction between ethylene carbonate and methanol using immobilized ionic liquids on MCM-41 (mesoporous molecular sieves) at 11.3 bar and 180 ˚C (Kim *et al.*, 2010) while a value of 81.2% is reported for the same reaction operated without any catalyst under supercritical conditions at 90 bar 250 ˚C (Feng *et al.*, 2005). This condition, however, has not considered in the current work.
- PC route: 1-15 bar for pressure; 0 ˚C to 200 ˚C for temperature. The low yields are confirmed by reported values for this route (Wei *et al.*, 2003).

The calculated DMC yields are compared with known experimental values in Figures 5.3, 5.4 and 5.5, for the urea-route, the EC-route, and the PC-route, respectively.

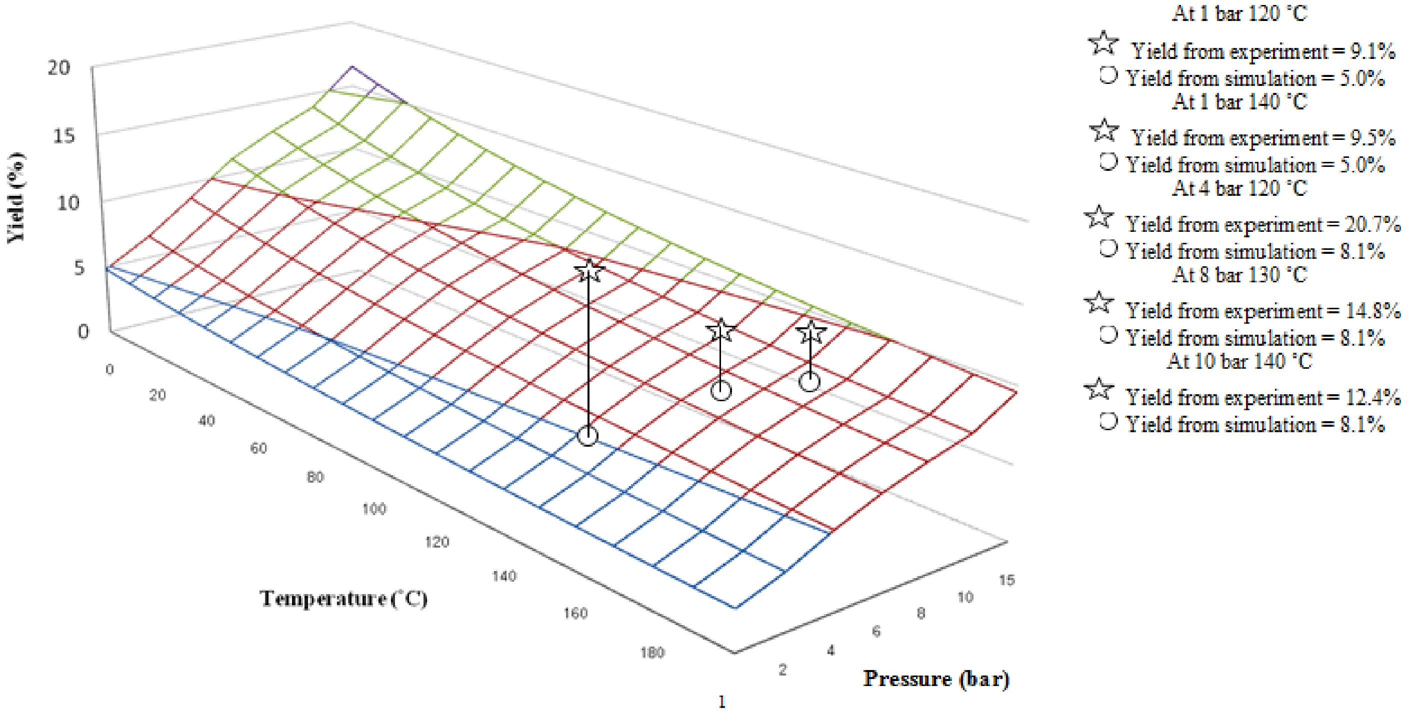


Figure 5.3 - DMC yield from the propylene carbonate route (Propylene carbonate: Methanol = 1:2)

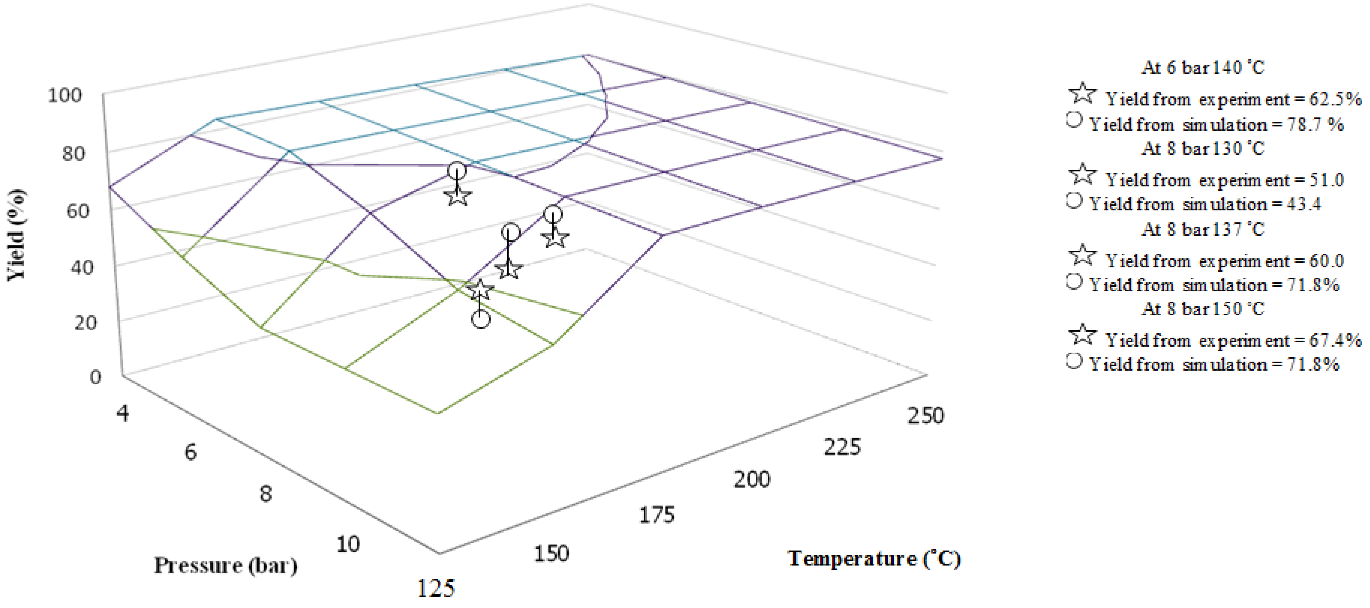


Figure 5.4 - DMC yield from the urea route (Urea: Methanol = 1:2).

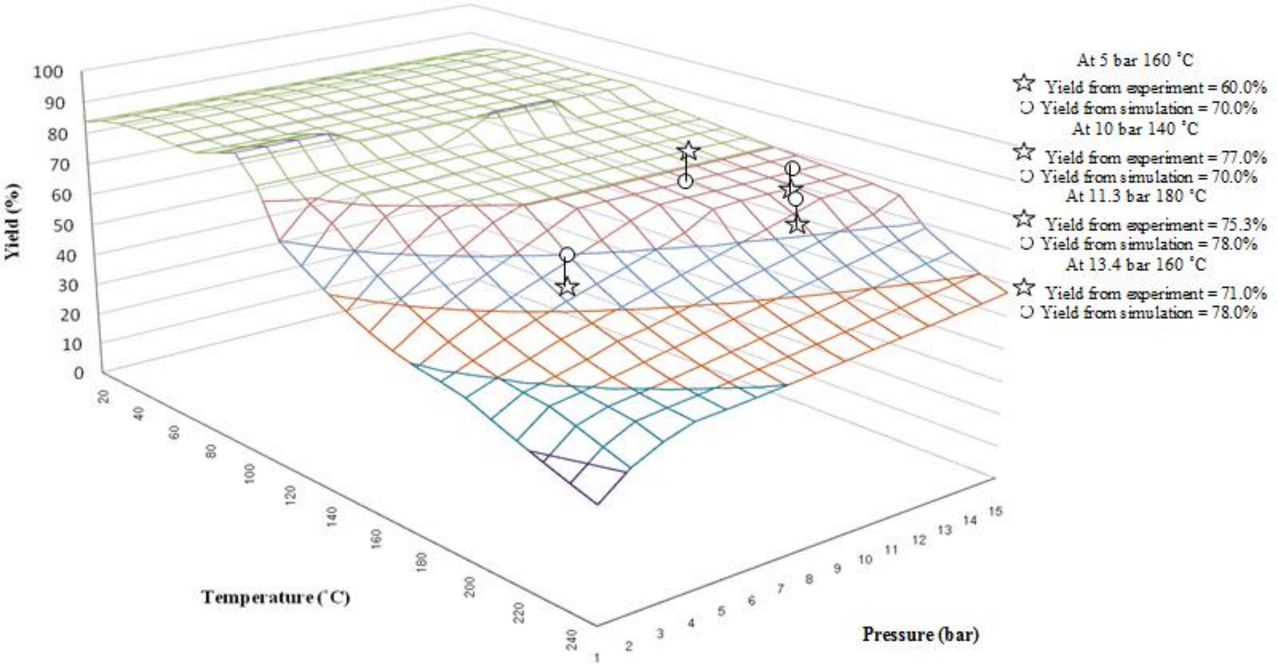


Figure 5.5 - DMC yield from the ethylene carbonate route (ethylene carbonate: Methanol = 1:2).

From the calculated values as well as the known experimental values, it is clear that the yields of DMC from the urea-route and the EC-route are much higher than the PC-route. The highest yields of DMC are 78.7% for the urea-route and 78% for the EC-route, while for the PC-route, the yield is only 5-20%. Based on these results, the EC-route together with the urea-route are retained for further detailed analysis instead of the PC route.

Therefore, the urea-route and the EC-route are selected for further investigation and analysis together with the BAYER-process. Also, these two CO_2-based alternatives are interesting because others have also studied the production of DMC from the urea-route (Wang *et al*., 2009; Zhang *et al*., 2012) and from the EC-route (Kim *et al*., 2010; Jagtap *et al*., 2008; Yang *et al*., 2010; Feng *et al*., 2005; Zhang *et al*., 2012) under different conditions (kinetics and supercritical condition) and catalysts (chemical and ionic liquids).

5.4 Preliminary Performance Evaluation

Because of the concerns on issues such as the depletion of natural resources, environmental-safety-health impacts, as well as sustainability of the chemical process, it is not enough to simply find the optimal chemical process converting given raw materials to specified products. It is necessary to also make the process sustainable. In this work, the well-known sustainability metrics (Azapagic, 2002; Carvalho *et al*., 2008) together with life-cycle assessment factors and some green chemistry indicators have been used. Three principal criteria, in addition to the process requirements have been selected for purposes of comparison. These are the energy consumption for unit product (at a specified purity), net CO_2 emission, the atom efficiency and the life-cycle assessment factors (global warming potential, carbon footprint, measure of toxicity, etc.). Many industries and businesses these days have better awareness on the environment issues. Consequently, life cycle assessment has become a key factor for establishing more sustainable options in process design and synthesis. So, the final design in terms of a selected set of performance criteria, such as amount of raw material used per kg of product or the amount of energy used per kg of product, are compared for all feasible alternatives. The systematic methodology for evaluating process alternatives for DMC production includes 4 key performance indicators based on the following criteria: energy consumption, net CO_2 emission, atom efficiency and life cycle assessment.

5.4.1 Methods and tools used

The work-flow (method) used to calculate the selected set of performance criteria is as follows:

Step-1: identify a process design for the selected process (it is assumed that a base case design is available for each process considered)
Step-2: perform the process simulation
Step-3: calculate the energy consumption, atom efficiency
Step-4: calculate the life-cycle assessment factors and the net CO_2 emission
Step-5: perform the overall analysis

5.4.1.1 Process simulation

Steady state process simulation has been performed with Aspen Plus®. For the reactor, the Gibbs free energy based equilibrium model has been employed. For distillation columns, the RADFRAC model has been used. The details of the thermodynamic models used are given in the corresponding simulation results (see section 5.4.2). The process simulation results include mass and energy balances for each process.

5.4.1.2: Energy consumption

The energy consumptions in all equipment are calculated from the steady state simulation results and these are summed to obtain the net energy consumption (MJ/hr) per unit mass of DMC product (kg/hr). This is in accordance with the definitions of sustainability metrics (Azapagic, 2002; Carvalho *et al*., 2008). The reaction/separation ratio (R/S), defined here as the ratio between the energy consumption in reaction parts and that in separation parts of the process, is also considered as a performance indicator. Low R/S ratio is usually caused by reaction with low product yield, which consequently requires high energy in downstream separation processes.

5.4.1.3: Atom efficiency

Atom efficiency is a criterion that considers efficiency of a reaction in terms of atoms of reacting substances that are present in the desired product. The process that generates by-product or contains side-reaction is considered having low atom efficiency. For example, in urea synthesis according to Eq. 5.5 in Table 5.1, carbon atom in the feed stream is converted to urea, while only 4 atoms of hydrogen from the reactants are found in urea. Therefore, the atom efficiency of C atom is 78.7%, while that of H atom is only 24.7% because H atom was loss to form by-product water compound which reduce atom efficiency of urea synthesis reaction.

5.4.1.4: Life cycle assessment

The issue of environmental impact is considered for the evaluation of the process alternatives. LCSoft (Piyarak, 2012; Kalakul *et al*., 2014) which is a computer aided tool for generation of LCA factors, has been used in this work. LCSoft performs the life cycle assessment, using US-EPA and IPCC emission factors to calculate the environmental impact for a given process. The performance evaluation of process alternatives are established in terms of carbon footprint (CF), which is the overall amount of carbon dioxide and other greenhouse gas emissions associated with one kilogram of product. The carbon footprint is related to other indicators such as the global warming potential (GWP) in term of kg of CO_2 equivalent. From a health and safety points of view, indicators such as the human toxicity-carcinogenic (HTC) in term of kg of benzene equivalent, human toxicity potential by exposure both dermal and inhalation (HTPE) in unit of time-weighted averages (1/TWA) are also considered (Kalakul *et al*., 2014).

5.4.1.5: Net CO_2 emission

Since one of the main goals in this work is to identify DMC production processes that have low impact on environments, CO_2 emissions from all associated processes for each synthesis route are calculated and compared. That is, the CO_2 created (or used) from the reactions is considered together with those generated (emitted) because of the use of energy. Therefore, in this work, it is assumed that all energy utilized as heat energy in all unit operations is obtained from complete combustion of methane, which releases 1 mol of CO_2 per 1 mol of methane combustion and provides a heating value of 889 MJ/kmol. Therefore, the total CO_2 emission in each DMC processing route is represented in term of CO_2 emission per one unit mass of DMC product (kg of CO_2/kg of DMC).

5.4.2 Process simulation and design analysis

Here, the two CO_2-based processes, that is, the urea-route and the EC-route are evaluated in terms of the selected performance criteria and compared with the commercial BAYER process. The design of the BAYER process is taken from the available data (Kricsfalussy *et al*., 1996).

5.4.2.1: Urea route

The process flowsheet for this process is highlighted in Figure 5.6, where it is shown that the process is divided into two sections: 1) the urea synthesis section and 2) the DMC synthesis section. The extended electrolytic UNIQUAC equation has been used to describe the non-ideality of liquid phase of NH_3–CO_2–H_2O–urea system under high pressure and high temperature, and the perturbed-hard-sphere (PHS) equation of state has been used to predict the vapor fugacity coefficients have been used to represent the VLE of CO_2-NH_3-urea system (Zhang *et al*., 2005).

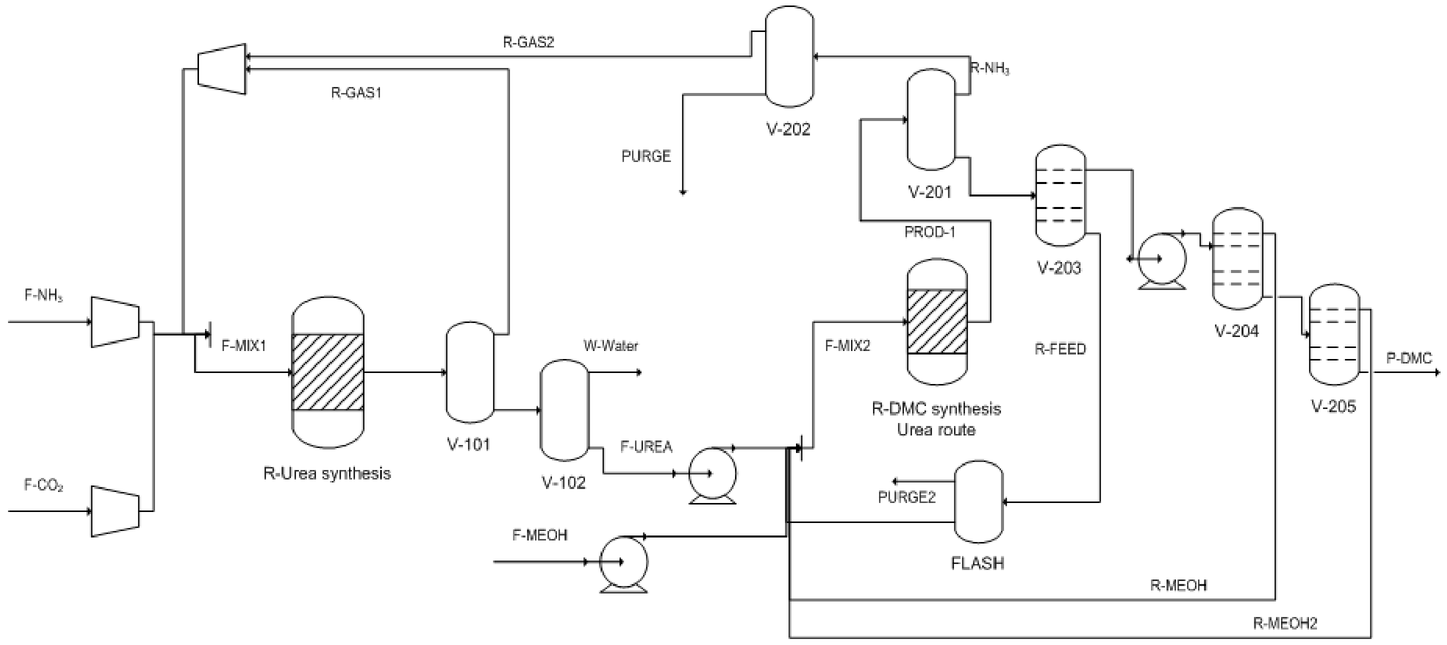


Figure 5.6 - Process flow diagram for the urea route for dimethyl carbonate production.

Section 1: Urea is synthesized from ammonia and carbon dioxide in the first reactor (R-Urea synthesis). Similar to the analysis of reaction 6 (see Table 5.1) and Figure 5.4, the conditions of operation for the synthesis of urea from CO_2 has been investigated for ratio of 4.25:1 for NH_3:CO_2. The calculated urea yields at equilibrium are shown in Figure 5.7. It can be noted that it is possible to achieve a yield of 73.8% when operating at P = 180 bar and T = 160 ºC. This conclusion agrees well with known experimental data (yield = 70%) reported by Zhang *et al* (2005). The reaction product stream flows into separator V-101 for recovery and recycle of the unreacted raw materials. The urea stream is sent to separator V-102 to purify urea by eliminating water.

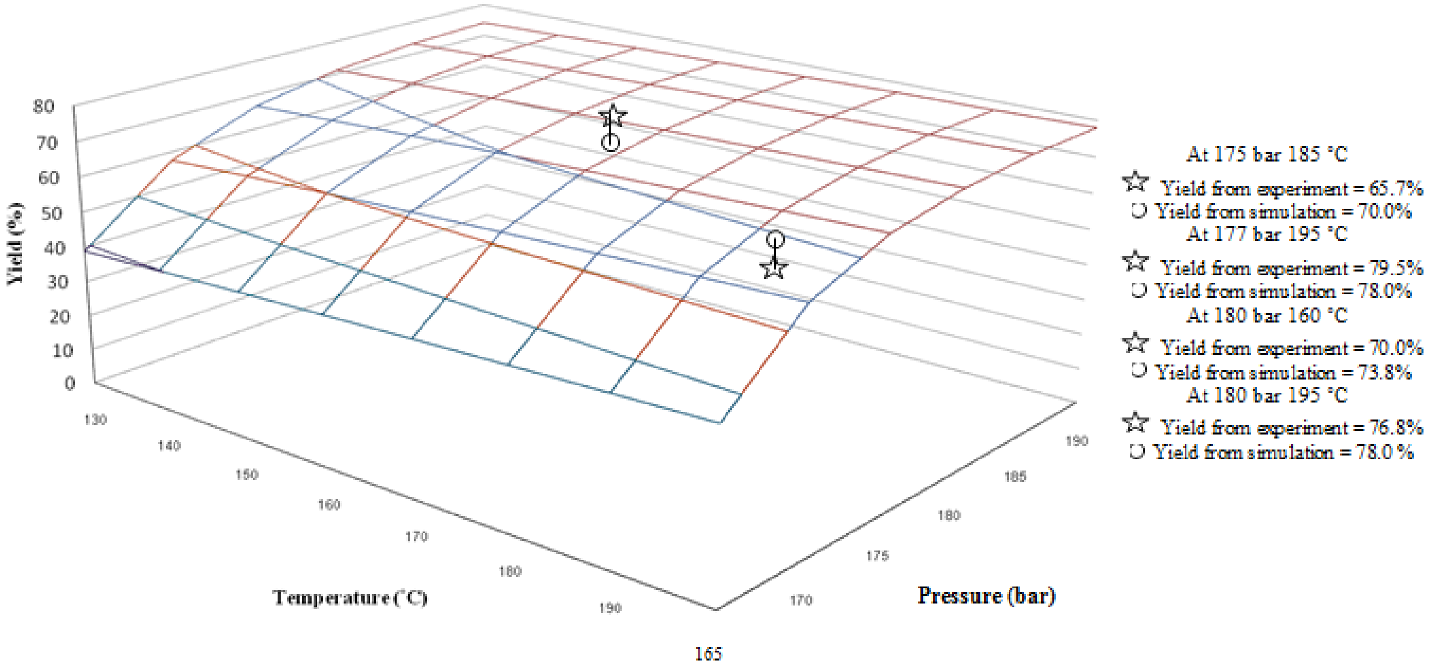


Figure 5.7 - Sensitivity analysis of urea production from CO$_2$ and NH$_3$

Section 2: In this section, the urea and methanol react to produce dimethyl carbonate. An equilibrium reaction is assumed. The energy consumption and yield of DMC are the key performance parameters for evaluation of optimum process condition. The reaction temperature slightly affects the yield of DMC, and so it is fixed at 140˚C (sees Figure 5.4). The operating pressure is varied between 1-20 bar and the pressure corresponding to the minimum energy usage is selected which correlate well with known experimental data (Sun, 2005). The results from process simulation, which confirms the reported experimental data, are shown in Figure 5.8, where the yield of DMC and the corresponding energy usage are plotted as a function of pressure.

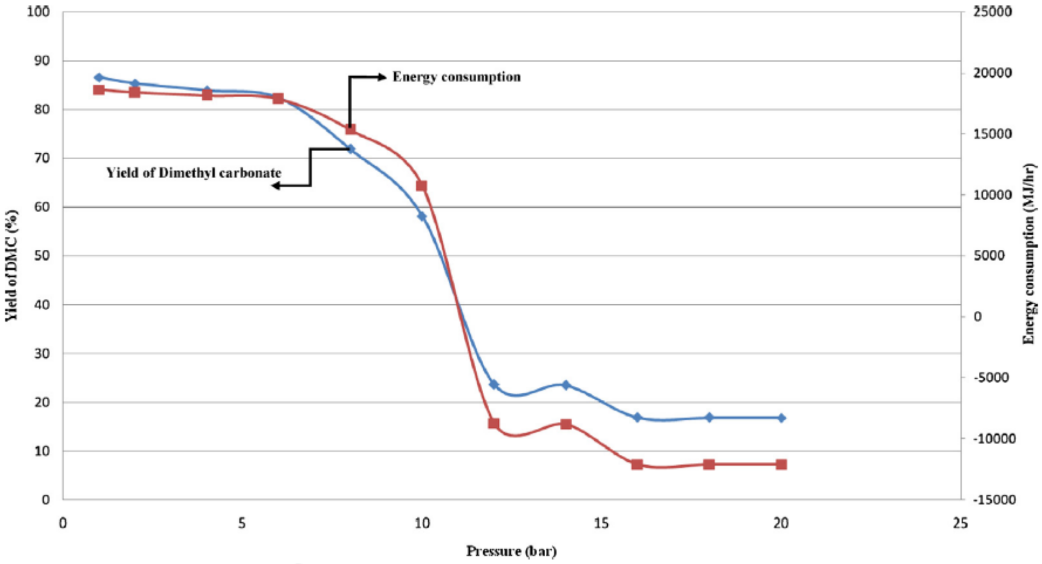


Figure 5.8 - Effect of pressure on DMC yield and energy consumption in urea transesterification process.

A feed molar ratio of MeOH:urea = 8 in the reactor (R-DMC) has been reported (Sun *et al*., 2005). The effect of methanol/urea molar ratio on the DMC yield has been studied by increasing it from 8 to 14. If the molar ratio of methanol/urea is lower than 8, the urea and MC (methyl carbamate) concentration is higher, the side reactions (the reactions of MeOH with urea) significantly reduces the DMC formation rate. Higher methanol/urea molar ratio therefore is desirable in order to increase the DMC yield. However, when the molar ratio of methanol/urea is higher than 14, the DMC yield begins to fall. Hence, a methanol/urea molar ratio of 8 was selected for this work.

The product stream (PROD-1) contains DMC, ammonia, unreacted of urea, methanol and small amount of methyl carbamate is sent to the V-201 to flash NH_3 gas and then the bottom stream is sent to V-203 to separate the unreacted urea. The effluent distillate stream from V-203 contains 12435 kg/hr of MeOH and 4366 kg/hr of DMC and sent to a series of pressurized distillation column (V-204 and V-205). The azeotropic mixture of DMC and MeOH is pressure dependent, and therefore, distillation columns V-204 and V-205 are used in a pressure-swing configuration with the pressure of V-204 and V-205 fixed at 30 and 20, respectively. The first column (V-204) is operated at 30 bar and the distillate (MeOH) stream is recycled (R-MeOH; 12279 kg/hr of MeOH and 478 kg/hr of DMC) to the reaction section and the bottom stream from V-204 (156 kg/hr of MeOH and 3887 kg/hr of DMC) is sent to the V-205 for purifying the DMC product. The V-205 column operates at 20 bar and gives a DMC product of 99.7 wt.% purity as bottom stream (P-DMC; 3.51 kg/hr of MeOH and 3773 kg/hr of DMC), while the distillate stream (R-MEOH2; 152 kg/hr of MeOH and 114 kg/hr of DMC) is recycled to the DMC synthesis section.

The important variables from the process simulation of the DMC production process through the urea-route are given in Table 5.2.

Table 5.2 - Mass balance simulation results for the production of DMC through the urea transesterification process and CO2 conversion.

	F-MIX1	F-MIX2	F-UREA	PROD-1	R-MIX	W-WATER	R-MEOH	R-MEOH2	R-FEED	P-DMC
Temperature (°C)	304.8	133.4	191.4	140	129	65	184.9	167.5	80.9	221.7
Pressure (bar)	180	8	1	8	8	1	30	20	1	20
Vapor Fraction	1	0.174	0	0.929	0.22	0	0	0	0	0
Mole Flow (kmol/hr)	420.95	581.66	63	581.66	6.03	74	388.63	6.03	40	42
Mass Flow (kg/hr)	9343.85	20783.44	3783.5	20783.44	266.98	1380.229	12759.76	266.98	1811.72	3776.93
Volume Flow (M^3/hr)	1264.26	451.74	3.31	2322.35	5.82	1.52	22.91	0.39	1.76	5.37
Enthalpy (MJ/hr)	-42467.6	-136649.4	-20166.8	-121168.6	-1757.2	-19120.8	-86.0	-1757.2	-11129.4	-23806.9
Mass Flow (kg/hr)										
CO_2	3520.78	0	0		0	0.062	0	0	0	0
NH_3	5790.39	1.43	0	1510.35	0	142.16	1.43	0	0	0
UREA	0.107	3783.49	3783.49	1122.28	0	60.06	0	0	1122.28	0
WATER	3.07	0.002	0.002	0.002	0	1152.97	0	0	0.002	0
MEOH	22.76	16405.59	0	13566.62	152.64	18.58	12279.69	152.64	679.08	3.51
DMC	6.73	592.92	0	4582.37	114.33	6.37	478.63	114.33	8.55	3773.42
Methyl Carbamate	0	0	0	1.80	0	0	0	0	1.80	0

5.4.2.2: Ethylene carbonate route

The base case design for DMC production based on the EC-route is illustrated in Figure 5.9. The PSRK model (Müller *et al*., 2013, Smith, 2005) is used for the calculation of vapor-liquid equilibrium, since for a system consisting of methanol, ethylene carbonate and ethylene glycol, use of this model has been reported by others (Gmehling *et al*., 2012). This process is also divided into two sections: 1) the ethylene carbonate synthesis section and 2) the DMC synthesis section.

Section 1: Ethylene carbonate is synthesized from ethylene oxide and carbon dioxide in the first reactor (R-EC synthesis). Similar to the analysis of reaction 5.10 (see table 5.1) and Figure 5.4, the conditions of operation for the synthesis of EC from CO_2 has been investigated for ratio of 2.4 for CO_2:EO. The calculated EC yields at equilibrium are shown in Figure 4.10. It can be noted that it is possible to achieve a yield of 84.73% when operating at P = 125 bar and T = 110 ˚C, which agrees well with experimental data (85.6%) reported by Lu *et al* (2004). The reaction product stream flows into separator V-101 for recovery and recycle of the unreacted raw materials. The ethylene carbonate stream is sent to DMC synthesis section through a pump.

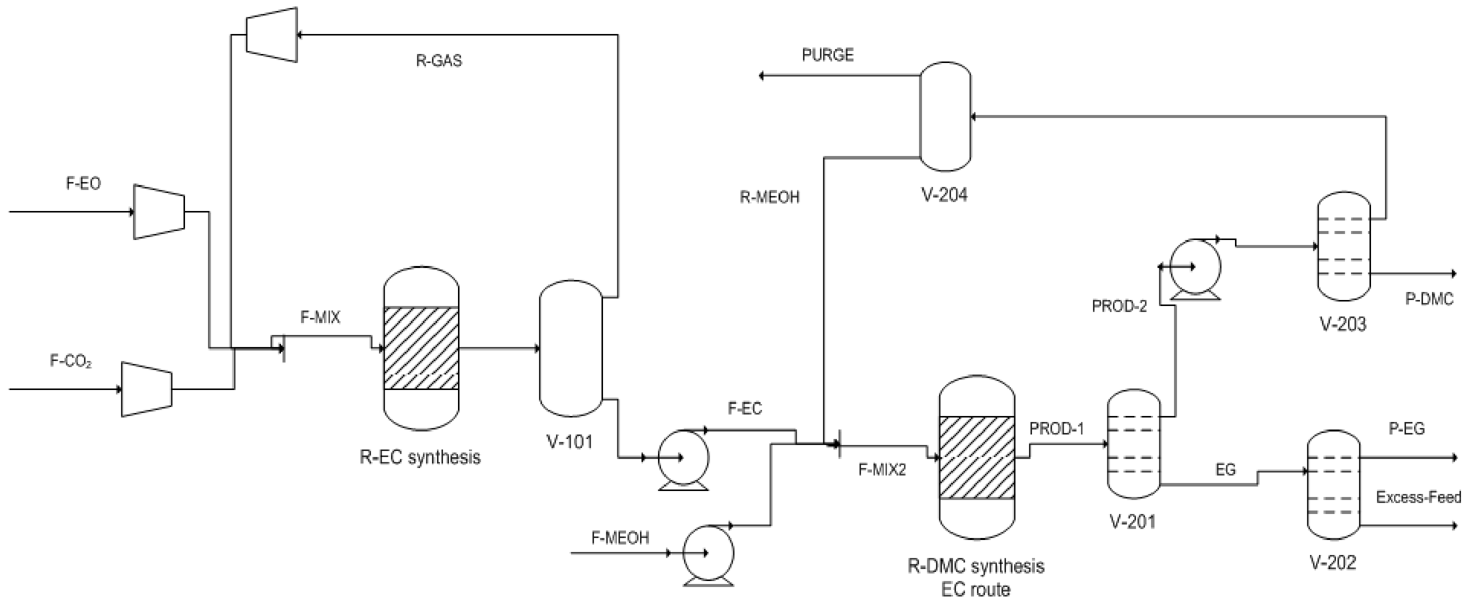


Figure 5.9 - Process flow diagram for the ethylene carbonate route for dimethyl carbonate production.

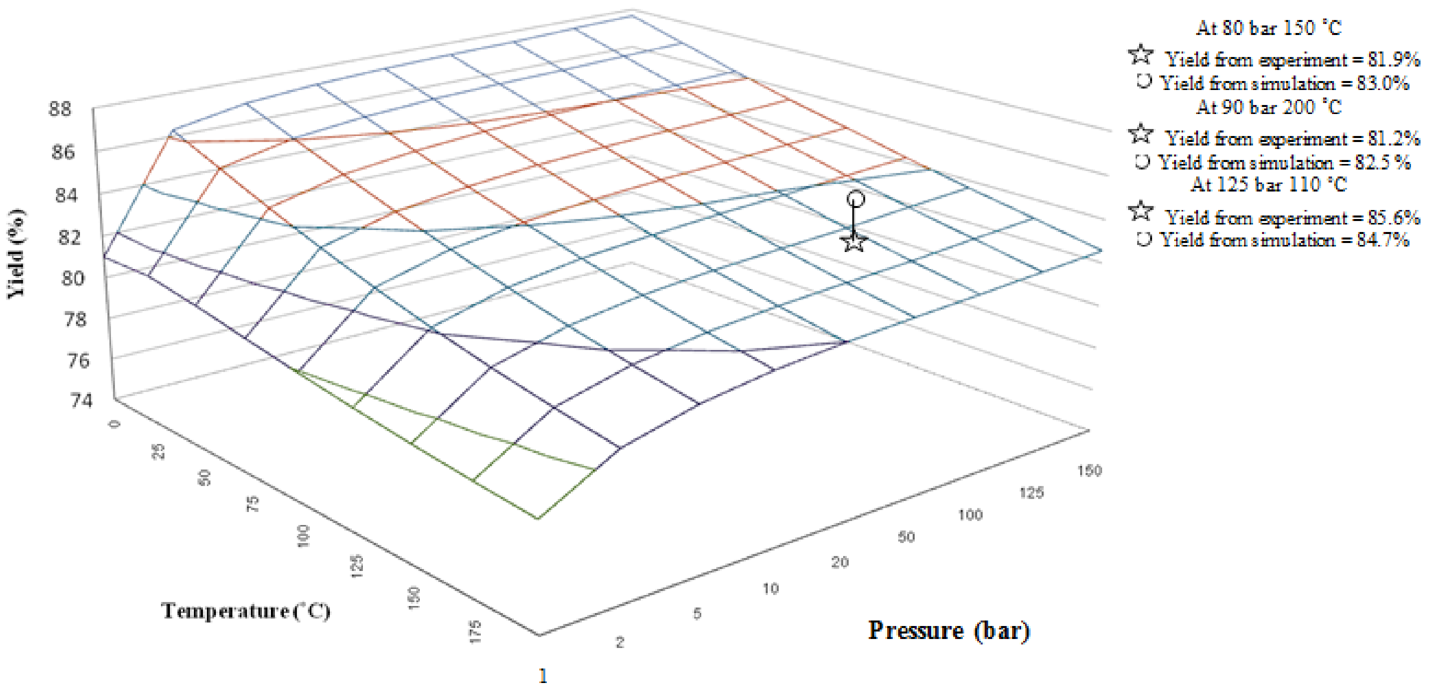


Figure 5.10 - Sensitivity analysis of ethylene carbonate production from CO_2 and ethylene oxide

Section 2: In this section, the ethylene carbonate and methanol are reacted to produce dimethyl carbonate. An equilibrium reaction is assumed. The energy consumption and yield of DMC are the key performance parameters with respect to selection of the reactor operating condition. The reaction temperature slightly affects the yield of DMC from 140 ˚C to 170 ˚C, and so it is fixed at 160 ˚C (sees Figure 5.5). The operating pressure is varied between 1-20 bar (see Figure 5.11) and the pressure corresponding to the minimum energy usage is selected, matching the reported data (Kim *et al.*, 2010). In Figure 5.11, the yield of DMC and the corresponding energy usage are plotted as a function of pressure.

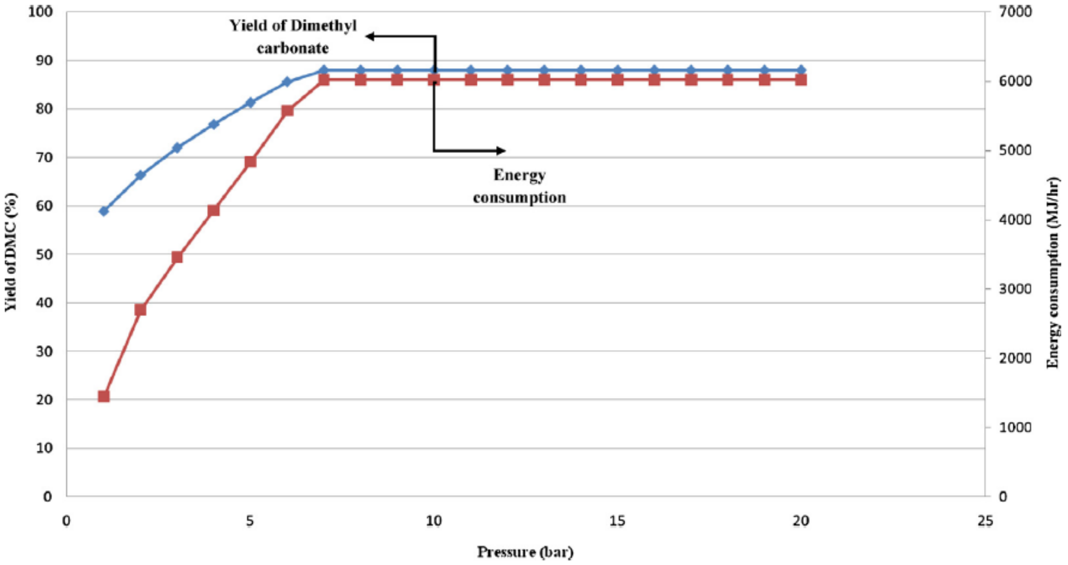


Figure 5.11 - Effect of pressure on DMC yield and energy consumption in ethylene carbonate transesterification process.

A feed molar ratio of MeOH:EC = 2.3 is sent to R-DMC, where a yield of DMC that matches with the reported value (Kim *et al.*, 2010) is obtained. The product stream (PROD-1) containing DMC, ethylene glycol (EG), unreacted of EC and MeOH is separated using the distillation column (V-201), operating at P = 10 bar. The distillate stream of V-201 (PROD-2) containing 1807 kg/hr of MeOH and 4215 kg/hr of DMC is sent to pressurized distillation column (V-203) from where, MeOH is recycle and the DMC product of specified purity is obtained. The stream R-MeOH, after the purge (V-204) contains 1795 kg/hr of MeOH and 258 kg/hr of DMC and the bottom stream of V-203 contains 3956 kg/hr of DMC at 99.2 wt.% purity as product.

The Ethylene glycol stream which is separated as bottom stream in distillation column (V-201) was sent to the distillation column (V-202) where the pressure is 10 bar. Here, 2731 kg/hr of EG is obtained as distillate stream at 96.05% purity (see Figure 5.9).

The important variables from mass and energy balance simulations of the DMC production process integrated with the EC plant is given in Table 5.3.

Table 5.3 - Mass balance simulation results for the production of DMC through the ethylene carbonate transesterification process and CO_2 conversion

	F-MIX	F-EC	F-MIX2	PROD-1	PROD-2	EG	P-EG	P-DMC	Excess Feed	R-MEOH
Temperature (°C)	588.7	248	154.9	160	141.2	306.1	294.5	220.3	319.7	165.9
Pressure (bar)	125.0	1	10	10	10	10	10	20	10	20
Vapor Fraction	1	0	0.185	0	0	0	0	0	0	0
Mole Flow (kmol/hr)	260.98	65	215	168.2	103.2	65	43.488	44.3	21.512	58.9
Mass Flow (kg/hr)	11708.70	5724.09	10530.42	10530.42	6022.86	4507.54	2731.1	3968.90	1776.44	2053.96
Volume Flow (M^3/hr)	149.60	5.19	151.90	11.80	7.60	5.15	3.27	5.62	1.84	3.35
Enthalpy (MJ/hr)	-68743.1	-34601.6	-67864.4	-69789.1	-40000.0	-28451.2	-178907	-25020.3	-10610.6	-13974.56
Mass Flow (kg/hr)										
CO_2	7921.76	0	0	0	0	0	0	0	0	0
Ethylene Oxide	3348.04	0	0	0	0	0	0	0	0	0
Ethylene Carbonate	438.90	5724.09	5724.09	1602.74	0	1602.74	107.72	0	1495.02	0
MEOH	0	0	4806.32	1807.17	1807.17	0	0	11.92	0	1795.25
DMC	0	0	0	4215.69	4215.68	0	0	3956.97	0	258.71
Ethylene Glycol	0	0	0	2904.80	0	2904.80	2623.27	0	281.42	0

5.4.2.3: BAYER process

The simulation of the BAYER process is based on the information provided in the patent (Kricsfalussy *et al.*, 1996). The process flow diagram is shown in Figure 5.12. The UNIQUAC model (Gmehling *et al.*, 2012) is used for the vapor-liquid equilibrium calculations. The partial carbonylation reaction of CO and MeOH is carried out in a reactive-distillation unit (Mohamed *et al.*, 2007; Simasatitkul *et al.*, 2013). Here, a gas-phase exothermic reaction is taking place where the excess reactant is removed, the equilibrium conversion shifted and azeotrope formations are avoided. The reaction temperature is known to vary between 120 ˚C to 300 ˚C, but values between 120 ˚C to 180 ˚C are preferred (Kricsfalussy *et al.*, 1996). The reaction is carried out at atmospheric pressure. However, to achieve a sufficiently high reaction rate, it is advantageous to carry out the reaction at a higher pressure, preferably between 10 to 50 bar, with the optimal between 12-22 bar. Water, which is formed from the reaction, is removed from the system, optionally after distilling off organics such as the DMC. In the zone of the reactive-distillation unit, molten salts, methanol and DMC are distilled off, together with small amounts of volatile by-products such as, formaldehyde and dimethyl acetal.

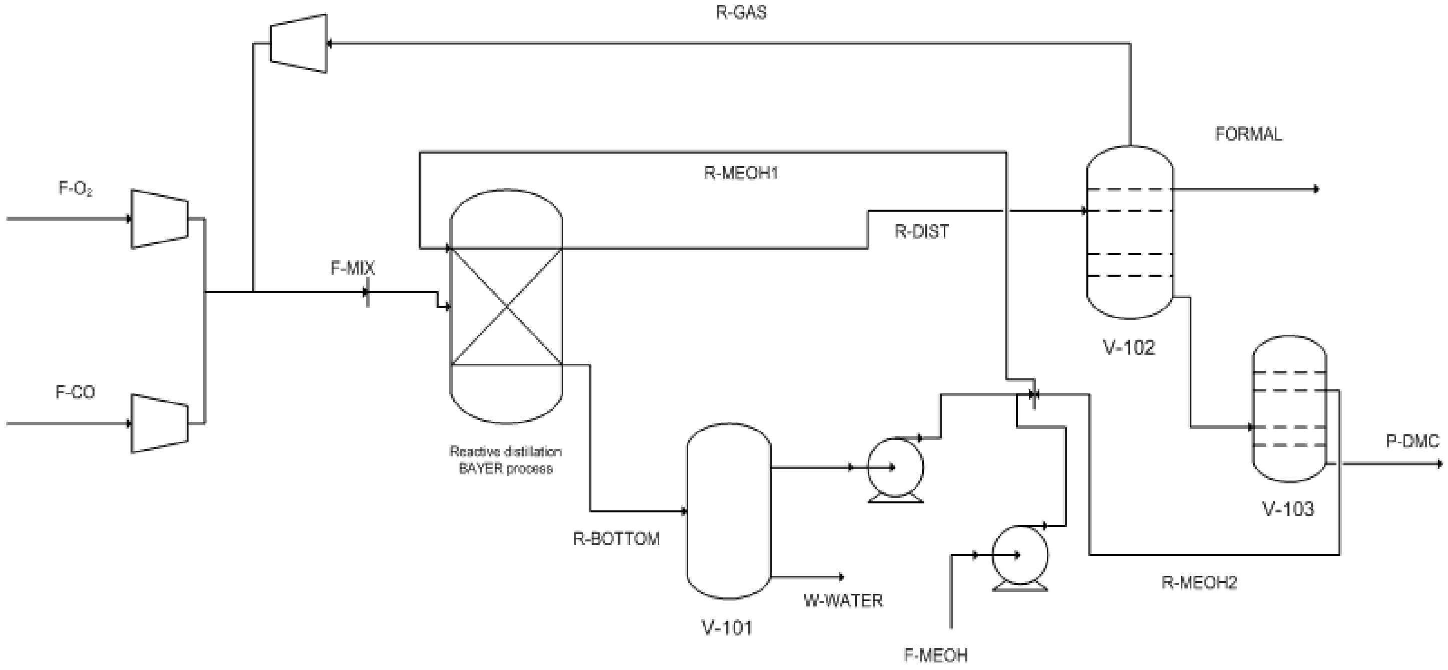


Figure 5.12 - Process flow diagram for BAYER process

Methanol introduced into the reaction zone contains relatively large amounts of DMC which, for example, has a composition corresponding to the MeOH/DMC azeotrope. It is possible to obtain a higher yield of DMC by shifting the equilibrium through the addition of excess MeOH. The Bayer process has also been simulated through Aspen Plus® using the reported design (Kricsfalussy *et al*., 1996). The simulation results are given in Table 5.4 and agree well with those reported in the patent, in terms of DMC yield of 99.5% and the process stream compositions.

Table 5.4 - Mass balance simulation results for the production of DMC through the BAYER process

	F-MIX	I-CO2	PURGE	R-BOTTOM	R-DIST	R-MEOH1	W-WATER	P-FORMAL	P-DMC
Temperature (°C)	401.90	25	25	150	150	35.8	98.5	25	183.3
Pressure (bar)	20	1	10	20	20	20	1	10	10
Vapor Fraction	1	1	1	0	0.93	0	0	0	0
Mole Flow (kmol/hr)	187.35	10.60	11.66	45.29	169.56	95.90	44.38	3.15	43
Mass Flow (kg/hr)	7148.26	466.65	493.67	853.34	9502.11	3242.50	828.95	179.64	3873.39
Volume Flow (M^3/hr)	525.75	262.85	28.90	0.99	281.27	4.05	0.90	0.2	4.90
Enthalpy (MJ/hr)	-43095.0	-4142.1	-3932.96	-12593.8	-66985.8	-23890.6	-12510.16	-1129.6	-24811.1
Mass Flow (kg/hr)									
CO	1267.30	0	0.76	0	7.60	0	0	0.003	0
O_2	1193.89	0	50.88	0	509.05	0	0	0.25	0
CO_2	4444.99	466.65	442.03	0	4444.99	0	0	24.61	0
Water	0	0	0	802.97	0	12.85	790.11	0	
MEOH	35.94	0	0	7.92	71.34	2951.06	4.74	35.39	0
DMC	14.67	0	0	42.44	4202.21	278.58	34.09	43.92	3873.39
FORMAL	191.45	0	0		266.90	0.009		75.44	0

5.4.3 Comparison of DMC production alternatives

5.4.3.1: Energy consumption

The simulated energy consumption in the DMC production process, for the urea-route this is found to be 59.36 MJ/kg-DMC. The simulated energy consumption in the EC-route is found to be 8.76 MJ/kg-DMC. The energy consumption in the BAYER-process is found to be 10.55 MJ/kg-DMC. In terms of energy consumption, DMC synthesis from urea-route is found to have high energy consumption due to the large molar ratio of MeOH:urea that is employed to shift the reaction equilibrium in the R-DMC reactor and the energy consumption in the downstream separation of the azeotrope mixture of MeOH/DMC.

5.4.3.2: Atom efficiency

Table 5.5 gives details of the atom efficiency calculations for the three process alternatives. Since the DMC production section is common to all 3 process alternatives, only this section is compared in terms of atom efficiency, energy requirement and net CO_2 emission.

Table 5.5 - Atom efficiency analysis of various DMC production processes

Process	Atom of substance in feed				Atom of substance in product				Atom efficiency%
	C	H	O	N	C	H	O	N	(C,H,O,N)
BAYER	137	368	148.5	0	129	258	129	0	(94.1, 70.0, 86.8, 0)
Urea-DMC									
Urea	80	1020	160	340	63	252	63	126	(78.7, 24.7, 39.3, 37.0)
DMC and NH$_3$	575	2300	575	126	125.7	517.2	125.7	88.6	(21.8, 22.4, 21.8, 70.3)
EC - DMC									
EC	332	304	436	0	195	260	195	0	(58.7, 85.5, 44.7, 0)
DMC and EG	345	860	345	0	219.7	527.4	219.7	0	(63.6, 61.3, 63.6, 0)

Considering atom efficiency (Table 5.5) of the two CO_2-based processes, it is found that the atom efficiency of the EC-route has higher values(C: 63.6, H: 61.3, O: 63.6, N: 0) than the urea-route (C: 21.8, H: 22.4, O: 21.8, N: 70.3) because ethylene glycol is considered as a valuable by-product from the petrochemical industry. Also, since the urea-route requires high feed molar ratio, its atom efficiency of the process is reduced. Moreover, in the urea synthesis step, water is generated as by-product and need to be removed from the process. This is done through V-102, but leads to loss of urea in the W-WATER stream. For BAYER process, which uses partial carbonylation of CO, the formation of water is considered as waste and needs further treatment. The atom efficiency of this process is higher than the CO_2 based processes: (C: 94.1, H: 70.0, O: 86.8, N: 0).

5.4.3.3: Net CO_2 emission

Table 5.6 compares the process alternatives in terms of energy consumption and the net CO_2 emission together with information on production rates, product purity and break-down of energy usage in different unit-operations in the process flowsheet. In terms of energy consumption per one unit of product, the DMC production section in the EC-route gives the lowest value (8.76 MJ/kg) compared to the BAYER process (10.55 MJ/kg) and the urea-route (59.36 MJ/kg). The high energy consumption in DMC production from urea-route is due to the excessive amount of methanol in the reaction-loop (as explained above). Comparison of the reaction and separation (R/S) ratios for the EC-route (0.058) and the urea-route (0.074) indicate that more energy is used in the separation section than in the reaction section due to recycle of large amounts of unreacted raw materials because of the low reaction conversion. The issue of CO_2 utilization in DMC production indicates that 1 mol of CO_2 is utilized for 1 mol of DMC and these processes generate CO_2 from utilities usage. In this work, it is assumed that captured CO_2 is pure and available on-site. The net amount of CO_2 emission is calculated on the basis of total CO_2 available in the feed stream (F-MIX= 7921 kg/hr: 180 kmol/hr). The CO_2 needed to produce ethylene carbonate as the intermediate is 5724 kg/hr (65 kmol/hr). This means that 2860 kg/hr (65 kmol/hr) of CO_2 is used for conversion to ethylene carbonate, which is then used to make 3968 kg/hr (44 kmol/hr) of DMC. The amount of CO_2 generated in overall process by utilities usage is 5692 kg/hr (129.37 kmol/hr). This indicates that this process actually reduces the CO_2 emission to atmosphere through utilization as raw material by 2860 kg/hr (65 kmol/hr). This means that the net CO_2 emission is 2832 kg/hr instead of 5692 kg/hr.

Another issue for use as measure for identifying a more sustainable process is the net CO_2 emission per one unit of product. The EC-route indicates the lowest CO_2 emission (0.433 kg of CO_2/kg-DMC), followed by the BAYER process (0.522 kg of CO_2/kg-DMC) and then the urea-route (2.938 kg of CO_2/kg-DMC). Considering the other important issues of environmental concern, it is found that the EC-route is less harmful to the environment, since there is a net reduction on the CO_2 emission (as CO_2 is used as a raw material). The net CO_2 emission of DMC production process by EC-route is thereby improved by 16.93% and global warming potential (GWP) is improved by 59.36% when compared to the BAYER process.

Table 5.6 - Performance comparison between BAYER, urea and ethylene carbonate processes for DMC production.

Performance Evaluation	Ethylene carbonate route	Urea route	BAYER process
Production evaluation			
DMC production rate	3968.90	3776.93	3873.39
DMC purity (%)	99.2	99.7	100.0
By-product production rate	2731.1	0	0
By-product purity (%)	96.05	0	0
Energy evaluation			
-Energy usage in DMC section (MJ/hr)			
Energy usage in reaction unit	1916.0	15510.0	12366.0
Energy usage in separation units	32812.17	208509.0	25734.0
Energy usage in utilities units	42.59	133.33	2,787.0
Reaction : Separation ratio	0.058	0.074	0.48
-Energy usage in CO_2 utilization section (MJ/hr)			
Energy usage in reaction unit	15748.0	7794.0	0
Energy usage in separation units	56588.0	35212.0	0
Energy usage in utilities units	7911.0	5122.0	0
Energy efficiency			
Energy usage in DMC production section (MJ/hr)	34770.7	224153.0	40888.0
Energy usage per kg of product (energy usage in DMC production section MJ/kg of DMC)	8.76	59.36	10.55
Total kg of CO_2 emission in DMC production section (referred to CH_4 combustion to provide energy 889 MJ/kmol of CH_4)	1720.9	11094.0	2023.0
CO_2 emission per one unit of DMC (kg/kg)	0.433	2.938	0.522
Total energy consumption (MJ/hr)	115017.7	272283.0	40888.0

5.4.3.4: LCA factors

The human toxicity by exposure and carcinogenic compound emission (HTC) and human toxicity potential by exposure both dermal and inhalation (HTPE) of EC route is reduced by 99.9% because BAYER process uses CO which is considered as a toxic and hazardous chemical. These results are shown through a radar-chart in Figure 5.13 where the BAYER process forms the boundary of the radar and the EC-route falls inside the radar for all criteria considered.

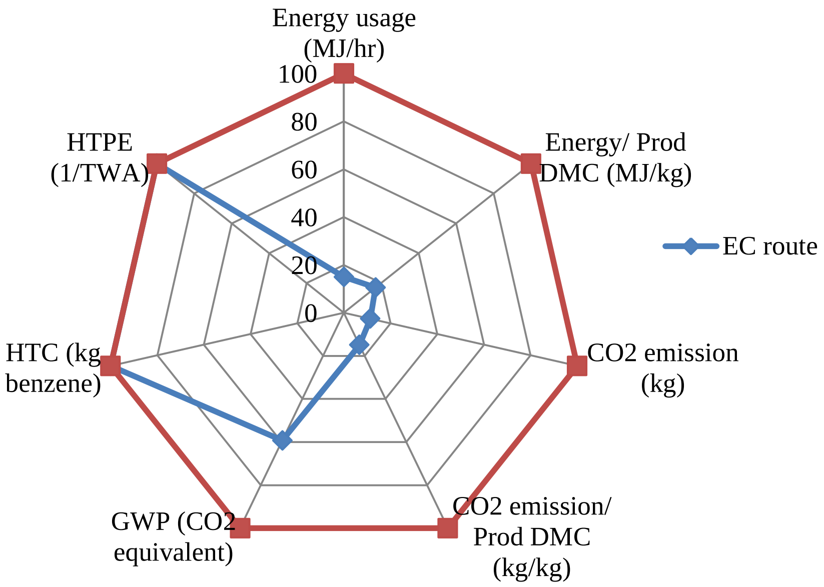


Figure 5.13 - Percent improvement in Performance indicators of important issues.

5.5 Conclusion

Different processes for DMC production based on CO_2 utilization have been investigated. The processes include the direct route of reacting CO_2 with methanol and indirect routes of converting CO_2 with ammonia, ethylene oxide and propylene oxide to urea, ethylene carbonate and propylene carbonate, respectively, and then further reacting them with methanol to DMC. Although the values of Gibbs free energy indicate advantage for the conventional processes (phosgene route, carbonylation of CO route and methyl nitrile route) against all of the CO_2-based processes, they become unattractive in regards to safety, toxicity and environment. The direct synthesis of methanol and carbon dioxide and the propylene carbonate routes are less promising than the other CO_2-based routes due to their higher Gibbs free energy values and lower DMC yields. By evaluating the three process alternatives of DMC production, that is, the ethylene carbonate route, the urea route and the BAYER process in terms of atom efficiency, energy consumption and net CO_2 emission, it is found that the ethylene carbonate route is the most promising process alternative for DMC production. Note that, however, the three processes considered in detail as well as those not considered may be further improved through process intensification and/or change of process conditions. .

Finally, the analysis given in this work is valid for the reported base case designs. Other important issues, such as detail economic analysis, the optimization, catalyst performance improvement to achieve the higher yield, activity, selectivity and stability leading to easier downstream separation have also not been considered. Also, new reactor design options, such as multi-functional reactor for reduced energy consumption and improved product yield by shifting the reaction equilibrium need to be further investigated. Moreover, improve the key performance indicator which can handle and use systematic methodology to achieve more sustainable process design. In this chapter, the cost for CO_2 recovery and purification unit, raw materials cost, capital investment cost, waste treatment and operating cost have not been considered. A more complete analysis could include the CO_2 source as well as a complete reaction tree together with options to further improve alternatives through opportunities for process intensification will be involved in the next chapter.

CHAPTER VI

SYSTEMATIC METHODS AND TOOLS FOR DESIGN OF SUSTAINABLE CO_2 UTILIZATION NETWORK FOR DIMETHYL CARBONATE PRODUCTION

Here, after the preliminary study of CO_2 utilization to DMC production stage, the CO_2 based DMC production process is considered to illustrate the application of implemented framework for more sustainable process synthesis- design-intensification of CO_2-utilization based chemical process.

Step 1. Problem definition

The product is DMC, and to produce it, CO_2 must be used as a feedstock. Therefore, information on all known technologies where CO_2 may be used to produce DMC is necessary. The CO_2 to be used is assumed to be available from CO_2 capture processes. The available data of DMC production such as price of raw materials, capital cost, utilities cost, waste treatment cost, etc., are needed for step 2. The obtained DMC specification is set at a purity higher than 99 wt.%. The best process alternative will be established in terms of *max profit* which considered sale price, raw material cost, capital investment cost, utilities cost and waste penalty cost.

Step 2. Data collection and superstructure definition

This work investigates DMC production from CO_2 via transesterification with methanol. This can be achieved via direct reaction between CO_2 and methanol to form DMC. Also via indirect routes, in which CO_2 is first utilized by the reaction with compounds such as ammonia (NH_3), ethylene oxide (EO), or propylene oxide (PO) to form chemical intermediates, i.e., urea, ethylene carbonate (EC), or propylene carbonate (PC), respectively. Then, DMC is produced by the transesterification of the intermediate with methanol. Available data for several DMC processing routes ranging from CO_2 direct synthesis, urea route, EC route and PC route are collected from reported technologies in the literature. For the direct use of CO_2 to produce DMC, it has been reported that CO_2 could react with methanol at critical temperature and critical pressure of CO_2 (Gu *et al.*, 2008). This direct transformation of CO_2 and methanol could avoid the use of toxic chemicals such as phosgene. Nevertheless, the direct utilization of CO_2 in commercial scale is challenging because CO_2 lies in a deep potential energy well of about −400 kJ/mol that requires huge amount of energy for activation (Sheppard *et al.*, 2003). On the other hand, other processes, such as urea-, EC-, or PC-routes are considered as new alternatives for integrating CO_2 utilization with the production of DMC.

The different catalysts applied for CO_2 utilization and DMC production can be classified as: alkali catalyst, acid catalyst, solid base catalyst and ionic liquids, which have been considered in the generation of multiple processing routes as shown in Table 6.1 where more data collected for the user interface is given and Table 6.2 for list of potential catalysts for DMC production by CO_2 based processes.

Table 6. 1 - The process interval inventory for generating superstructure. (Noted that the price of carbon dioxide in this research are neglected; the CO_2 specification is at high purity 99.99%wt)

Processing step	*No. interval*	*Process interval*
1. Raw materials	1.1	Fresh methanol (0.53 USD/kg)
	1.2	Carbon dioxide
	1.3	Hydrogen (4000 USD/kg)
	1.4	Nitrogen (0.05 USD/kg)
	1.5	Ammonia (0.33 USD/kg)
	1.6	Ethylene oxide (1.55 USD/kg)
	1.7	Ethylene carbonate (1.8 USD/kg)
	1,8	Propylene oxide (1.65 USD/kg)
	1.9	Propylene carbonate (1.4 USD/kg)
2. NH_3 synthesis	2.1	Ammonia synthesis (Yunusov *et al.*, 2004)
3. CO_2 coupling reaction	3.1	Urea synthesis 1 (Ono *et al.*, 1982)
	3.2	Urea synthesis 2 (Kojima *et al.*, 1999)
	3.3	Urea synthesis 3 (Zhang *et al.*, 2005)
	3.4	Ethylene carbonate synthesis 1 (Dai *et al.*, 2009)
	3.5	Ethylene carbonate synthesis 2 (Lu *et al.*, 2001)
	3.6	Ethylene carbonate synthesis 3 (Lu *et al.*, 2001)
	3.7	Propylene carbonate synthesis 1 (Li *et al.*, 2012)
	3.8	Propylene carbonate synthesis 2 (Wang *et al.*, 2012)
	3.9	Propylene carbonate synthesis 3 (Dai *et al.*, 2009)
4. Separation	4.1	Gas recovery (NH_3 and CO_2) 1
	4.2	Gas recovery (NH_3 and CO_2) 2
	4.3	Gas recovery EO 1
	4.4	Gas recovery EO 2
	4.5	Gas recovery EO 3
	4.6	Gas recovery PO 1
	4.7	Gas recovery PO 2
	4.8	Gas recovery PO 3
5. Purification	5.1	Dehydration of water from urea
	5.2	Crystallization of urea 1
	5.3	Crystallization of urea 2
6. Carbonate division	6.1	Urea division
	6.2	Ethylene carbonate division
	6.3	Propylene carbonate division
7. DMC synthesis	7.1	Direct CO_2 synthesis (Zhong *et al.*, 2002)
	7.2	DMC from urea1 (Lin *et al.*, 2004)
	7.3	DMC from urea2 (Sun *et al.*, 2005)

	7.4	DMC from urea3 (Wang *et al*., 2009)
	7.5	DMC from EC1 (Feng *et al*., 2005)
	7.6	DMC from EC2 (Jagtap *et al*., 2008)
	7.7	DMC from EC3 (Yang *et al*., 2010)
	7.8	DMC from one pot CO_2 and EO (Bhanage *et al*., 2001)
	7.9	DMC from PC1 (Williams *et al*., 2009)
	7.10	DMC from PC2 (Chang *et al*., 2004)
	7.11	DMC from one pot CO_2 and PO (Chang *et al*., 2004)
8. Separation	8.1	Separation gas1
	8.2	Separation NH_3 gas
	8.3	Separation R1
	8.4	Separation MeOH 1
	8.5	Separation MeOH 2
	8.6	Separation MeOH and EC
	8.7	Separation MeOH 3
	8.8	Separation MeOH 4
	8.9	Separation MeOH and PC
9. Purification	9.1	Separation Urea 1
	9.2	Separation Urea 2
	9.3	Separation EC 1
	9.4	Separation EC 2
	9.5	Separation EC 3
	9.6	Separation EC (one pot)
	9.7	Separation PC 1
	9.8	Separation PC 2
	9.9	Separation PC (one pot)
10. Purification	10.1	Separation Ethylene glycol
	10.2	Separation Propylene glycol
11. Pressurized purification	11.1	Azeotrope distillation 1
	11.2	Azeotrope distillation 2
	11.3	Azeotrope distillation 3
	11.4	Azeotrope distillation 4
12. Product	12.1	DMC (1.2 USD/kg)
	12.2	Urea (0.33 USD/kg)
	12.3	DMC and Ethylene glycol (1.2 USD/kg & 1.3 USD/kg)
	12.4	DMC and Propylene glycol (1.2 USD/kg & 1.4 USD/kg)

Table 6.2 - List of potential catalysts for DMC production by CO_2 based processes.

Raw material	**Alcohol**	**Catalyst**	**Molar Ratio**	**Temperature (°C)**	**Pressure (bar)**	**Yield (%)**	**Reference**
For CO_2 utilization							
CO_2+NH_3	-	-	1:3.9	195	171.6	70	Ono *et al.*, 1982
			1:2	185	175	90	Kojima *et al.*, 1999
			1:4	186	145	79.2	Zhang *et al.*, 2005
CO_2+EO	-	SalenCo(II)-MCM-41	-	110	125	85.6	Dai *et al.*, 2009
		SalenAlCl/*n*-Bu4NBr	-	10	250	30	Lu *et al.*, 2001
		SalenAlCl/*n*-Bu4NBr	-	30	250	96	Lu *et al.*, 2001
CO_2+PO	-	(TCPPCo(III)X/PTAT, X = CF3COO, OAc, Br, Cl)	-	25	12	80	Li *et al.*, 2012
		[Zn(BHBPDI)] and (TBAB)	-	110	40	97.8	Wang *et al.*, 2012
		Fe/porphyrin	-	80	7	73.5	Dai, Luo, Yin & Au, 2009

N_2+H_2	-	$K_2[Ru(CO)_4]$ + K		300	1	71	Yunusov *et al.*, 2004
For DMC production							
CO_2	Methanol	Cu–Ni/graphite	-	105	12	0.91	Bian *et al.*, 2009
		Ni–Cu/MoSiO	-	140	1	14.16	Zhong *et al.*, 2002
		Potassium methoxide (CH_3OK)		80	20	14.1	Cai *et al.*, 2009
Urea	Methanol	Dibutyltindimethyloxide	1:10	180	20	37.5	Lin *et al.*, 2004
		polyphosphoric acid	1:14	140	8	67.4	Sun *et al.*, 2005
		Et_3NHCl–$ZnCl_2$	1:36.6	160	1	26.4	Wang *et al.*, 2009
EC	Methanol	-	1:8	250	90	81.2	Feng *et al.*, 2005
		poly-4-vinyl pyridine	1:4	140	10	82	Jagtap *et al.*, 2008
		1,4diazobicyclo[2.2.2]octane	1:15	70	1	84	Yang *et al.*, 2010
PC	Methanol	Verkade superbase catalysed	1:20	45	1	70	Williams *et al.*, 2009
		K_2CO_3–KI/ZnO		150	165	43.4	Chang *et al.*, 2004
		KI/ZnO		150	165	36.8	Chang *et al.*, 2004
CO_2+EC	Methanol	MgO	-	150	80	66.1	Bhanage *et al.*, 2001

CO_2+PC	Methanol	K_2CO_3–KI/ZnO	-	150	165	57.9	Chang *et al.*, 2004

Based on the information collected, the superstructure of processing steps is generated (see Figure 6.6), where 10 processing steps with multiple intervals for each step have been used. There are 23 parameters including Molecular weight of component i (Mw_i), Composition of the feed ($\theta_{i,kk}$), transportation distance ($Dist_{k,kk}$), Transportation Price (USD km MT) ($Trans_{k,kk}$), superstructure ($S_{k,kk}$), Superstructure of primary outlet ($SP_{k,kk}$), Allocation of process interval to the different steps ($PS_{kk,step}$), split fraction ($\xi_{k,kk}$), waste fraction ($SW_{k,kk}$), ratio of chemical consumed in the reaction ($\alpha_{i,kk}$), ratio of chemical added ($\mu_{i,kk}$), Split factor ($\varepsilon_{i,kk}$), dollar price per feedstock per kg ($P1_{i,kk}$), dollar price of chemical and utilities per MT ($P2_i$), dollar price of product per kg ($P3_{i,kk}$), stoichiometric coefficient of products in reaction ($\gamma_{i,kk,rr}$), fraction conversion of the reactant ($\theta_{i,kk,rr}$), number of Raw Materials ($NRAW$), number of Processing Units ($NPROC$), Generic cost of wastes USD per MT ($WasteCost$), Flow points for piecewise linearization ($Fpoint_{\mathrm{j}}$), Coefficients for Capital piecewise linearization ($\alpha_{j,kk}$), Coefficients for Capital piecewise linearization ($\beta_{j,kk}$). In addition, there are 21 variables including inflow of component i to process kk coming from k ($F_{i,k,kk}$), mass flow after the mixing point ($F^{M}_{i,kk}$), mass flow after the reaction ($F^{R}_{i,kk}$), mass flow outside ($F^{out}_{i,kk}$), component mass flow in a interval ($F_{in_{\mathrm{i,kk}}}$), mass flow outlet from interval kk (used for capital calculation) ($F^{out}_{i,kk}$), mass flow primary outlet ($F^{out1}_{i,kk}$), mass flow secondary outlet ($F^{out2}_{i,kk}$), chemical use in interval kk ($R_{\mathrm{i,kk}}$), amount of waste produced (waste), total revenues (sales), cost for transportation from interval k to kk ($C_{Tr_{k,kk}}$), total transportation costs ($TransCost$), cost for raw materials ($rawcost$), cost for utilities ($utilcost$), cost for heating ($heatcost$), capital cost for equipment (Inv_{kk}), capital expenditure ($CAPEX$), penalty for waste production ($WastePenal$) and objective function ($Max\ profit$) and one binary variable, selection of process-intervals k (binary) (y_k).

Step 3. Mathematical programming problem

For each interval in Figure 6.2, the appropriate model equations are retrieved from Quaglia *et al.*, (2013) to obtain the full network model.

The MINLP problem is formulated with the simplified process model of Table 6.2 and solved in GAMS. The objective function for finding the optimal processing route is *Max profit* as given by Eq. (3.8). The summary of DMC production by CO_2 based processing problem formulation statistics is reported in Table 6.3.

Table 6.3 - Summary of the mathematical programming (MINLP) problem for DMC production by CO_2-utilization based processing steps**.**

Block of equations	37
Block of variables	24
Non-zero elements	144825
Single equations	50752
Single variables	53737
Discrete variables	5430

In this case study, the objective function (see Eq. (3.8)) is described by products sale price (DMC and by-products such as EG and PG), raw material cost (CO_2, nitrogen, hydrogen, ammonia, ethylene oxide, propylene oxide, ethylene carbonate, propylene carbonate and methanol), utilities cost (HP and LP steam, hot oil, cooling water and electricity), waste penalty (water treatment and gas emission) and capital investment. The results of MINLP problem indicate that the DMC production by urea route gives the maximum objective function value, and the second optimal processing route is the DMC production by EC route and the third is DMC production by PC route. These three processing routes are shown through the shaded intervals in Figure 6.2 and the determined values of the objective function for each processing route are given in Table 6.4.

Table 6.4 - Summary of the results from the MINLP solution

Issues	**CO_2 direct synthesis**	**DMC from Urea (1st rank)**	**DMC from PC**	**DMC from EC (2nd rank)**
Objective function (Max profit, USD/yr))	-76044817	24243436	13900692	19356971
Total sale price (USD/yr)	50827500	54646380 (DMC + NH_3)	106615860 (DMC + PG)	84412800 (DMC + EG)
Raw material Cost (USD/yr)	123033600 (CO_2 + MeOH)	21450240 (CO_2 + MeOH)	20653056 (CO_2 + MeOH)	19210880 (CO_2+ MeOH)
		25269120 (CO_2 + NH_3 + MeOH)	83803572 (CO_2 + PO + MeOH)	57341370 (CO_2 + EO + MeOH)
Utilities cost (USD/yr)	153379	632053	542496	517023
Capital investment cost (USD/yr)Project life 10 years	2727270	7163341	6315100	5437436
Transportation cost (neglected)	-	-	-	-
Waste penalty cost and use of hazardous materials	958068	1157310	2054000	1760000

(USD/yr)				
CO_2 utilization in overall process (kmol/h)	445	104	91.61	77.81

The simple process flowsheet for using in process interval in the DMC production through the urea route is shown in Figure 6.1.

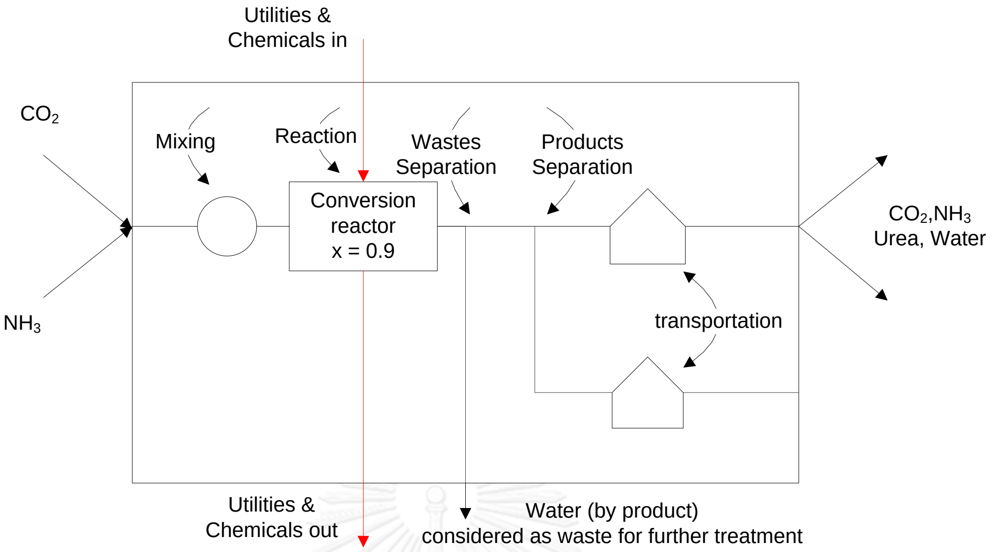


Figure 6.1 - The example of transformation data into mathematical model for using as input in process interval: GAMS generic code.

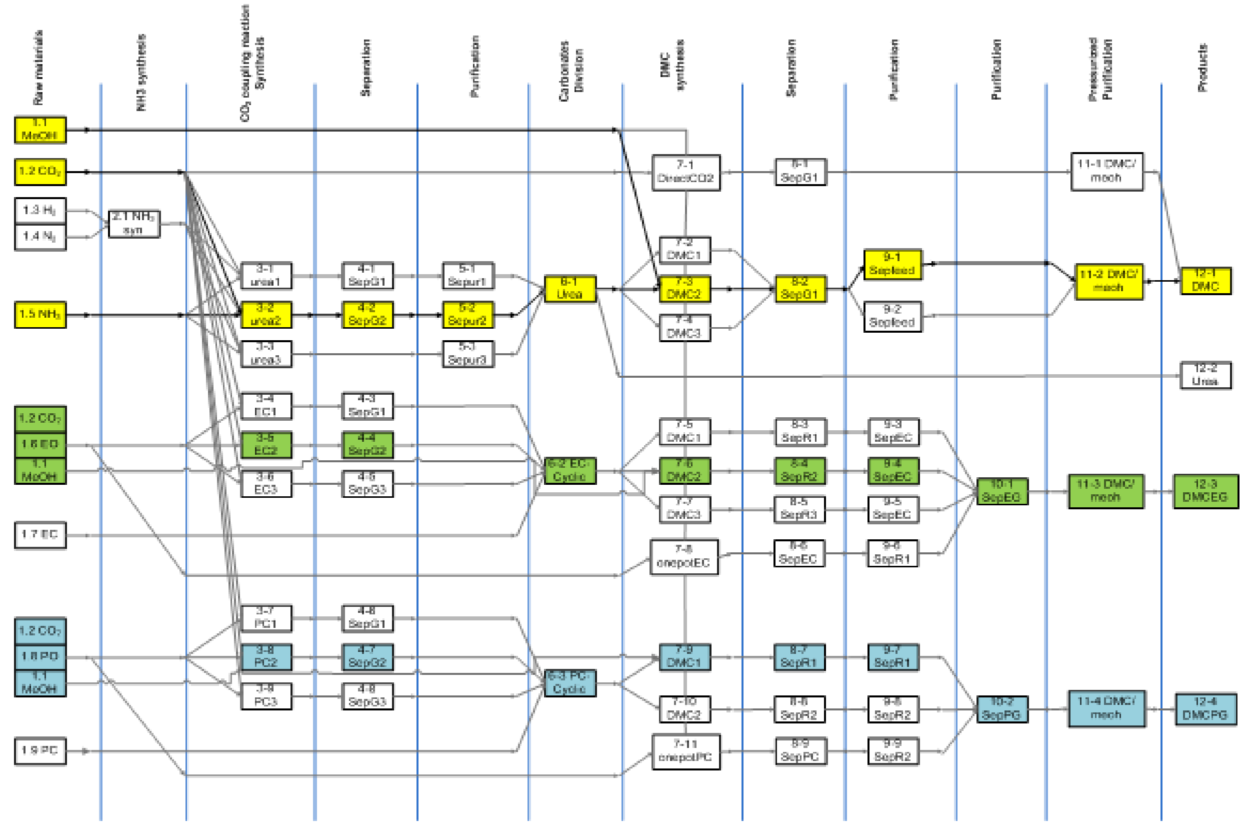


Figure 6.2 - Superstructure for DMC production network highlighting the optimal processing steps. Yellow indicates the optimal process configuration (urea route), light green indicates the second best (EC route) and light blue indicates the third best processing route (PC route).

Step 4. MINLP solution

The MINLP problem described above has been solved with GAMS (IBM Corp, 2009). On average, a typical MINLP needed 363 iterations and 3167 ms computing time on an Intel® Core™ i5-3230 CPU 2.60 GHz, RAM 8 GB, 64-bit operating system, Window 7 computer.

The MINLP solution results are given in Table 6.3 and are based on a DMC production rate of 62.75 kmol/h or 5647.5 kg/h (40662 MMT/yr). The best process candidate in the "synthesis" stage is DMC production via urea route, which offers the maximum profit of 24243436 USD/yr. The competitiveness of the EO and PO routes depends significantly on the price of petroleum. The equivalent profit can be achieved when the price of EO decreases from 1.55 to 1.415 USD/kg (9.7% reduction) and the price of PO decreases from 1.65 to 1.381 USD/kg (16.3% reduction), respectively. These routes earn more benefit from the sale of valuable by-products ethylene glycol (EG) and propylene glycol (PG). It should be noted that the best process candidate reported in our previous work (Kongpanna *et al*., 2015) was the EC route. The different results are mainly due to the use of a different objective function. In the previous work, only energy consumption, CO_2 emission and life cycle assessment were considered; however, in this study the main objective function is '*Max profit*' that includes raw material costs, fixed capital investment costs and waste penalty costs.

So, as base case design, the two best process flowsheets are used as process candidates: the DMC production by urea route and the EC route. Only the detailed results for the urea route are given for the next steps while the results of the EC route are included only in the analysis and assessment in step 9.

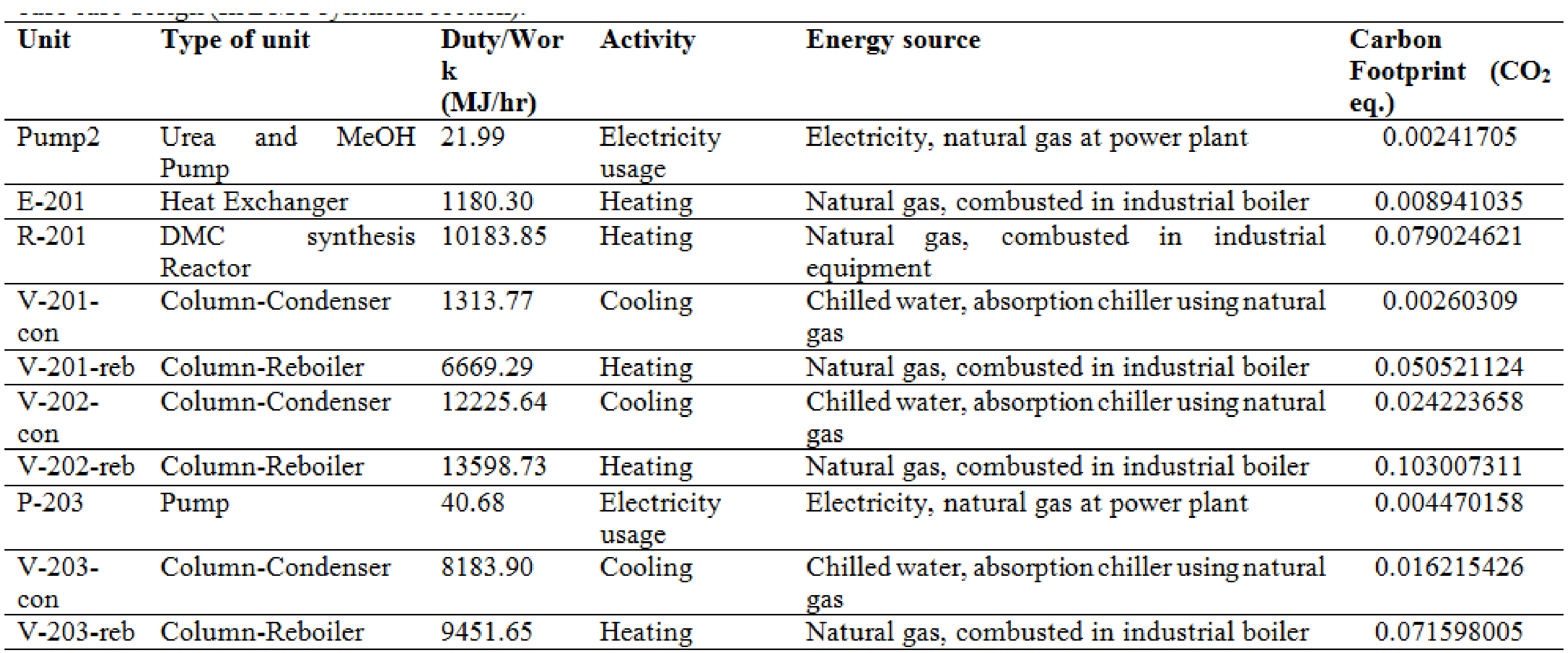
Step 5. Base case design

The DMC production route via urea highlighted in Figure 6.3 is the base case design. The process design is divided into 2 sections, the CO_2 utilization section which uses CO_2 and NH_3 as raw materials for producing urea and then urea is sent to the next section, the DMC synthesis section. Here, urea and MeOH react in the DMC synthesis reactor followed by a series of separation and purification steps to obtain the specified DMC product. The mass balance and design specification of all unit operations are given in Tables 6.5 and 6.6, respectively.

Table 6.5 - Mass balance simulation results for the production of DMC through the urea transesterification process and CO_2 conversion as base case design.

	CO_2FEED	NH_3FEED	MIixFeed1	FEEDR	P-UREA	F-UREA	F-MEOH	MixFeed2	R-MEOH	P-DMC
Temperature °C	25	25	169.2	25	200	184.3	25	75.5	136.3	179.4
Pressure bar	1	1	1	1	18	1	1	1	10	10
Vapor Fraction	1	1	1	1	0.38	0	0	0.101	0	0
Mole Flow kmol/hr	78.06	180.21	300	41.72	223.2	76.78	136.10	311.67	69.40	69.40
Mass Flow kg/hr	3435.49	3069.10	7807.09	1302.49	7807.09	4579.37	4361.08	13403.92	2539.39	6125.42
Volume Flow M^3/hr	1935.09	4467.30	11034.72	1034.35	192.69	3.97	5.5	923.47	3.74	7.68
Enthalpy MJ/hr	-30698	-8267.58	-46827.3	-9535.34	-54458.9	-24593.6	-32451.1	-85165.3	-17556.1	-39467.7
Mass Flow kg/hr										
CO_2	3435.49	0	4400.98	965.49	1021.02	0	0	0	0	0
NH_3	0	3069.10	3406.11	337	790.21	0.002	0	1.15	1.14	0
Urea	0	0	0	0	4612.27	4565.64	0	6005.56	0	0.002
H_2O	0	0	0	0	1383.57	13.72	0	14.24	0.27	13.72
Methanol	0	0	0	0	0	0	4361.08	6408.43	2046.57	39.73
DMC	0	0	0	0	0	0	0	974.52	491.40	6071.96

Table 6.6 - Unit operations specification for the production of DMC through the urea transesterification process and CO_2 conversion as base case design (In DMC synthesis section)



Unit	**Type of unit**	**Duty/Work (MJ/hr)**	**Activity**	**Energy source**	**Carbon Footprint (CO_2 eq.)**
Pump2	Urea and MeOH Pump	21.99	Electricity usage	Electricity, natural gas at power plant	0.00241705
E-201	Heat Exchanger	1180.30	Heating	Natural gas, combusted in industrial boiler	0.008941035
R-201	DMC synthesis Reactor	10183.85	Heating	Natural gas, combusted in industrial equipment	0.079024621
V-201-con	Column-Condenser	1313.77	Cooling	Chilled water, absorption chiller using natural gas	0.00260309
V-201-reb	Column-Reboiler	6669.29	Heating	Natural gas, combusted in industrial boiler	0.050521124
V-202-con	Column-Condenser	12225.64	Cooling	Chilled water, absorption chiller using natural gas	0.024223658
V-202-reb	Column-Reboiler	13598.73	Heating	Natural gas, combusted in industrial boiler	0.103007311
P-203	Pump	40.68	Electricity usage	Electricity, natural gas at power plant	0.004470158
V-203-con	Column-Condenser	8183.90	Cooling	Chilled water, absorption chiller using natural gas	0.016215426
V-203-reb	Column-Reboiler	9451.65	Heating	Natural gas, combusted in industrial boiler	0.071598005

Step 6. Rigorous simulation

The detailed process data for the urea route are obtained through process simulation and formed the basis for design decisions. The simulation of this base case involves 16 unit operations, 30 streams and 7 compounds (see Figure 5.3). The extended electrolytic UNIQUAC equation is used to describe nonideality of liquid phase, which is NH_3–CO_2–H_2O–Urea mixture under high pressure and high temperature, while the perturbed-hard-sphere (PHS) equation of state is used to predict the fugacity coefficients of the vapor in the VLE calculation of the CO_2-NH_3-Urea system (Zhang *et al.*, 2005). Missing binary interaction parameters for the UNIQUAC model in ASPEN simulator of the DMC/MeOH system were collected from literature reported by Holtbruegge *et al*., (2013).

Section 1 description (see Figure 6.3): Urea is synthesized from ammonia and carbon dioxide in the first reactor. This process can utilize 3435 kg/h of CO_2 coupling reaction with NH_3 3069 kg/h for producing 4612 kg/h of urea. The feed stream to reactor (with additional recycled stream) molar ratio of NH_3: CO_2 was 2:1. The simulation revealed a high urea yield of 76.8% when the reactor is operated at 180 bar and 200 ˚C. The value agrees well with the experimental data (70%) reported by Zhang, Zhang, Yao, & Yuan, 2005. The reaction product stream flows into separators V-101 and V-102 for recovery and recycle of the unreacted raw materials. The removal of water to obtain purified urea is done in a separator V-103.

Section 2 description (see Figure 6.3): In this section, urea and methanol reacted to produce DMC. The feed streams contain 4565 kg/h of urea and 4361 kg/h of MeOH and some of urea and MeOH which remain in the recycle stream. The reactor is operated at 140 ˚C and 8 bar, assuming equilibrium reaction. Yield of DMC achieved is 67.4%, which is relatively close to the reported experimental data (Sun *et al*., 2005). The product stream flows to the separation and purification section having azeotropic distillation for DMC/MeOH separation. The first column is a flash separator (V-201) employed to separate NH_3 gas for recycle to the urea synthesis section, the bottom stream contains the unconverted urea 1957 kg/h, MeOH 2087 kg/h and DMC 7046 kg/h. Then, the product stream is sent to the series of pressurized distillation columns (V-202 and V-203) to separate the azeotropic mixture of DMC/MeOH. The production rate of this base case design is 6071 kg/h (67.4 kmol/h) with the 99.11wt.% purity.

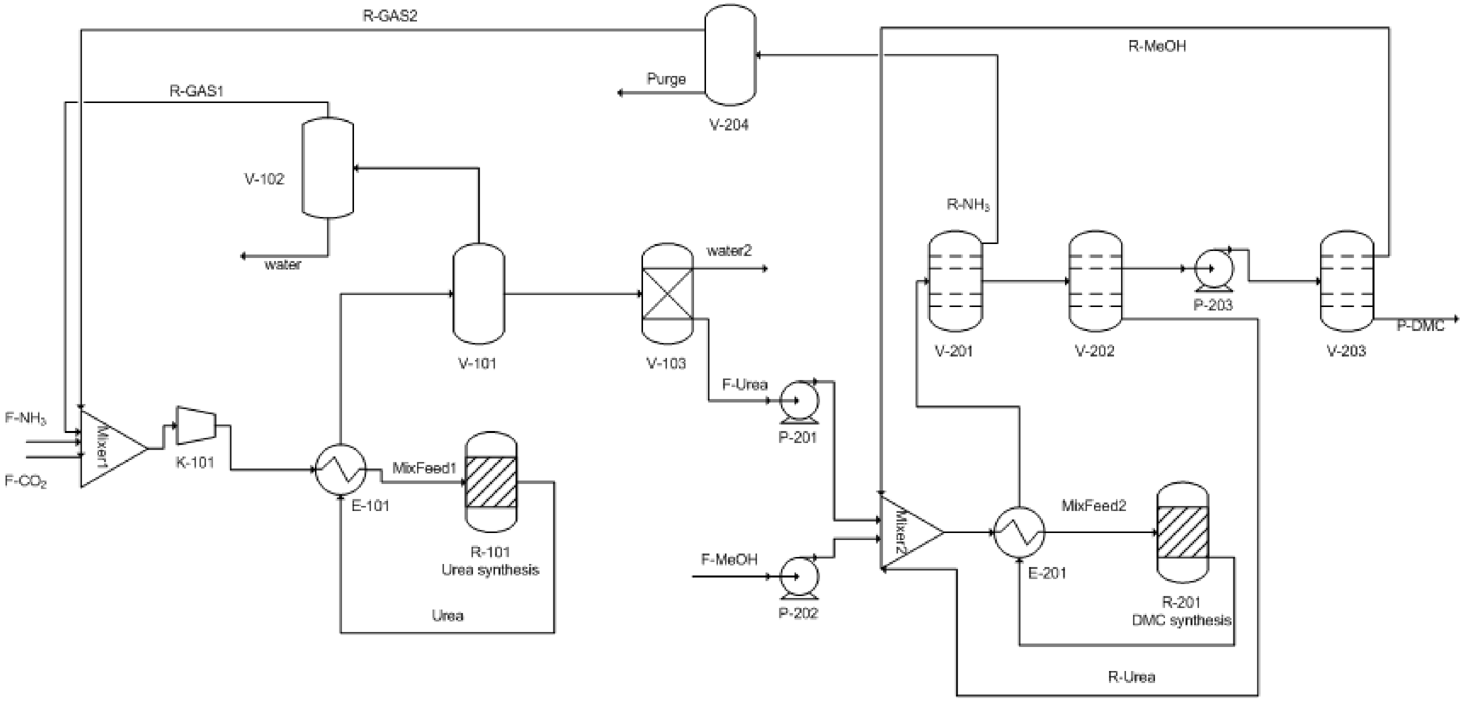


Figure 6.3 - The optimal DMC production process by urea route (base case design)

Step 7. Process analysis and target setting

The base case process design is further evaluated by SustainPro (Carvalho *et al*., 2008) to identify the process "hot-spots", that is, the locations in the process that have the highest potential for improvement. The hot-spots are found in the DMC production section are indicated in Figure 6.4 and also listed in Table 6.7.

It can be seen in Table 6.7 that there is high material loss (-TVA values) of methanol accompanied by energy consumption (+EWC values) in the open-paths (OP). Furthermore, high energy consumption is also observed in the given closed-path (CP) associated with methanol. It can be seen that the energy waste cost of OP12 and CP17 is large, comparing with other paths. The “Indicator sensitivity analysis” algorithm in SustainPro, which is capable of identifying the design targets as well as determining their desired target values, is used to identify the potential for significant improvements in the process. These identified indicators are designated as design targets for new process alternatives (Carvalho *et al*., 2008). The results given in Tables 6.8 and 6.9 indicate that there is high potential for improvement in OP12, the energy usage for methanol flow in open-path and CP17, the energy usage for methanol recirculating in the DMC synthesis section. So, the hot-spots of this process are the DMC synthesis reactor and the downstream separation of DMC/MeOH azeotropic mixture, which require high energy consumption for the separation task.

It should be noted that the closed-path (CP17) having the highest values of EWC is also considered as a bottleneck (see Figure 6.4).

Table 6.7 - List of identified „"hot-spots"" in the open-paths and closed-paths in the DMC processes of Figure 6.4.

Path (No.)	**Component**	**Flowrate (kg/h)**	**MVA (10^3 USD/yr)**	**EWC (10^3 USD/yr)**	**TVA (10^3 USD/yr)**	**Design sensitivity analysis (%improvement)**
OP12	MeOH	1309.95	-565.01	215.68	-780.69	High
OP13	MeOH	648.380	-281.00	195.09	-476.09	High
OP7	Urea	2677.82	-1.928	184.10	-186.02	High
OP15	DMC	6072.00	28298.16	156.45	28141.71	Low
CP17	MeOH	2089.10	0	1004.32	-1004.32	High
CP15	Urea	1957.80	0	33.63	-33.63	Low
CP18	DMC	974.53	0	25.06	-25.06	Low

Table 6.8 - The indicator sensitivity analysis results for the open-paths.

OP12	**Improvement (%)**		
Variable variation (%)	F-MeOH	V-202	R-201 DMC synthesis reactor
5	3.47	0.00	5
10	7.05	0.00	10
15	10.75	0.00	15

Table 6.9 - The indicator sensitivity analysis results for the closed-paths.

CP17	**Improvement (%)**	
Variable variation (%)	R-201 DMC synthesis reactor	Flow CP-17
5	5	4.27
10	10	8.60
15	15	13.00

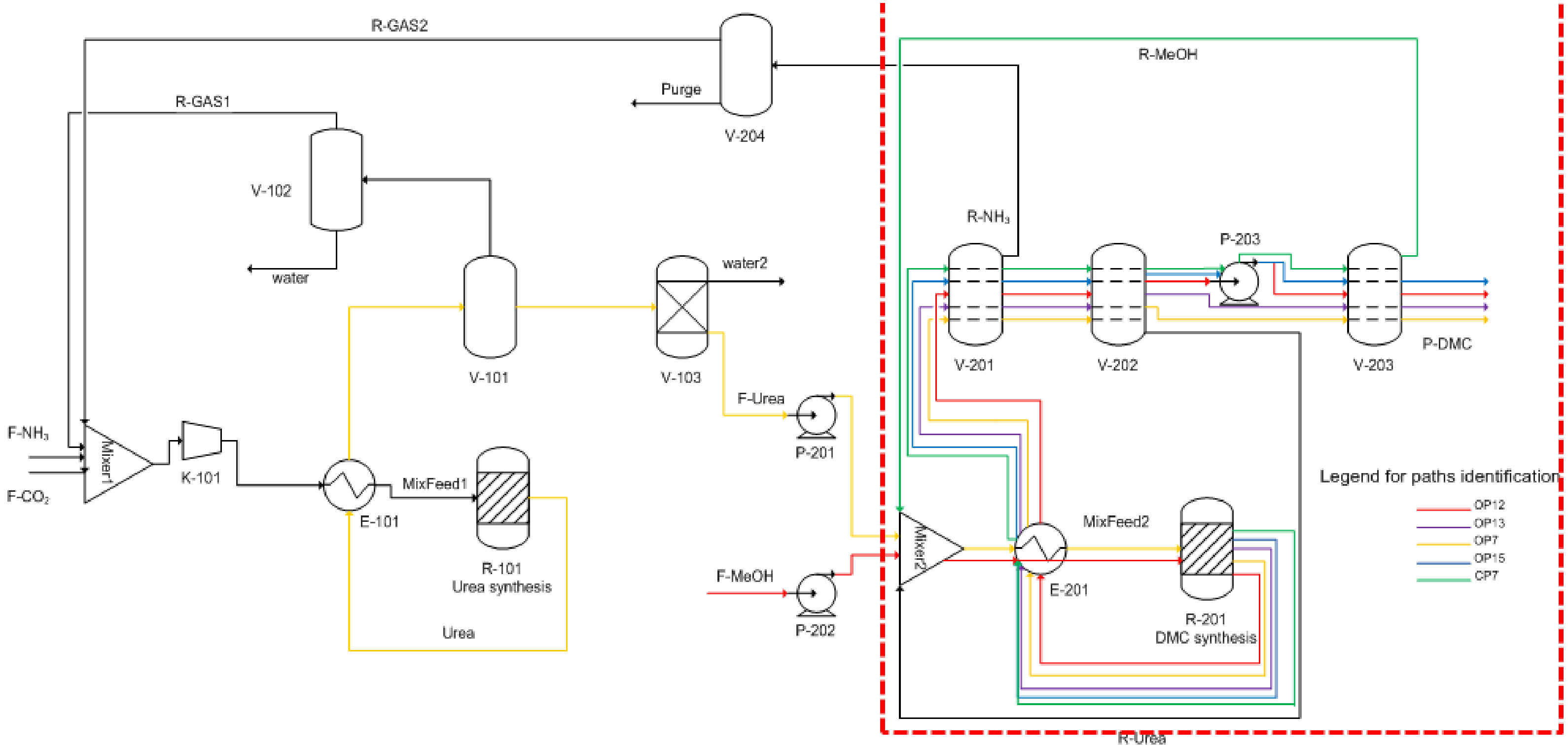


Figure 6.4 - Identification of open-path and closed-path having major bottlenecks in the process flowsheet.

Table 6.10 - Results from preliminary evaluation of the base case design.

Sustainability metrics	
Total energy consumption (MJ/h)	86710.92
Energy consumption in CO_2 utilization section (MJ/h)	23841.80
Energy consumption in DMC synthesis section (MJ/h)	62869.12
DMC production (kg/h)	6071.96
Energy consumption/kg of product DMC (MJ/kg)	10.35
Economic indicators	
Total sale prices (USD/yr)	52461734.4
Total cost (USD/yr)	33064514.0
Net profit margin (USD/yr)	19397220.4
Fixed-capital Investment (USD/yr)	7163341.0
Operating cost (USD/yr)	632053.0
Raw material cost (USD/yr)	25269120.0
Cooling water usage (GJ/yr)	194954.4
Fuel usage (GJ/yr)	295783.2
Life cycle assessment indicators	
CO_2 emission / kg of product DMC	1.281
HTC / kg of product DMC	0.0003
GWP / kg of product DMC	2.256

The economic and life cycle assessment analyses were also updated for the base case after rigorous simulations. The results are given in Table 6.10, which are used in step 9.

The paths OP12 and CP17 are identified as process bottlenecks with respect to TVA, MVA and EWC are located in the path of the DMC synthesis reactor (R-201), and series of separators (V-201, V-202 and V-203). The process bottlenecks occur due to the reaction equilibrium (with low conversion) and separation of azeotropic mixtures, requiring thereby a large amount of energy to separate the ternary mixture of urea/DMC/MeOH and the binary azeotrope mixture of DMC/MeOH. Therefore, the DMC synthesis reactor and the downstream separation of DMC/MeOH azeotropic mixture in the DMC synthesis section were taken as the target of the process debottlenecking. Based on economic and sustainability analysis, the process performance improvement must be made and matched with the target indicator for achieving more sustainable process. Therefore, the new process alternatives need to match the following target indicators;

- Reduction in process separation energy consumption.
- Improvement in process sustainability factors.
- Improvement in process economic & life cycle assessment indicators.
- Reduction in waste generation (by-product formation).
- Reduction utilities consumption and waste generation in the overall process.

Step 8. Alternative generation

The objective of this step is to generate process alternatives that match the design targets: higher yield of DMC in the DMC synthesis reactor and reduced energy consumption in downstream separation of DMC/MeOH to obtain more sustainable designs.

8.1. Problem and objective function definition

Problem definition: The identification of more sustainable (innovative) process designs for the production of DMC through the improvement in economic and sustainability.

The objective function: To specify the best process alternatives which respect to sustainability metrics, economic and life cycle assessment indicators. The LCSoft and ECON are using as the performance evaluation tools to achieve more sustainable process alternative than base case design. The equation for the objective function in process alternative evaluation is the "*Net profit margin*" which shown in Eq. (6.1)

$$Net\ Profit\ Margin = Total\ Sale\ Prices - Total\ Cost \qquad (6.1)$$

- Total sale prices- calculated from products prices (USD/kg) x production rate (kg/yr).
- Total cost- calculated from fixed capital cost (USD/yr) + operating cost (utilities) (USD/yr) + Raw material cost (USD/yr).

8.2. Analysis of the process

Data from steady-state mass and energy balances are collected from the rigorous simulation results of base case design. The DMC synthesis reactor and the downstream separation of DMC/MeOH azeotropic mixture in the DMC synthesis section were taken as the target of the process debottlenecking (see step 6 and 7). Thus the generation of (more sustainable) intensified flowsheet alternatives is performed on the DMC synthesis section (red dotted box) as shown in Figure 6.4.

The base case design flowsheet is first transformed (Siirola, 1996) into a task-based flowsheet (Figure 6.5) and then into a phenomena-based flowsheet (Figure 6.6) where the tasks (representative of the unit operations) are decomposed into phenomena building blocks (Lutze *et al*.,2013; Babi *et al*., 2015) that verify the application of a task. These phenomena building blocks are derived from the analysis of chemical/bio-chemical processes where it has been found that most processes can be represented by 9 individual PBBs. These are mixing (*M*), heating (*H*), cooling (*C*), reaction (*R*), 2 phase mixing (*2phM*), phase contact (*PC*), phase transition (*PT*), phase separation (*PS*) and dividing *(D)*.

The PBBs identified for the base case design (initial set of PBBs) are: M, 2phM, H, C, R, PC(VL), PT(VL), PS (VL) and D, where VL represents vapor-liquid.

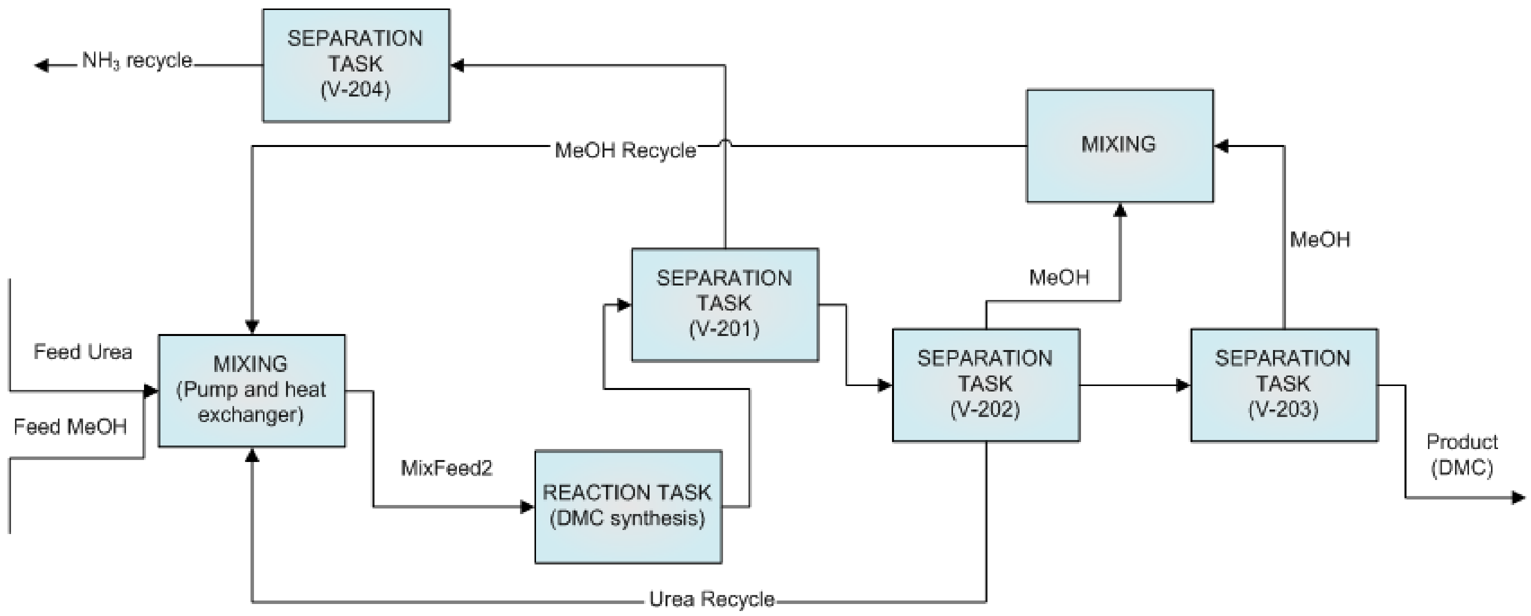


Figure 6.5 - Task-based representation of the base case flowsheet for DMC production by urea route (Siirola, 1996).

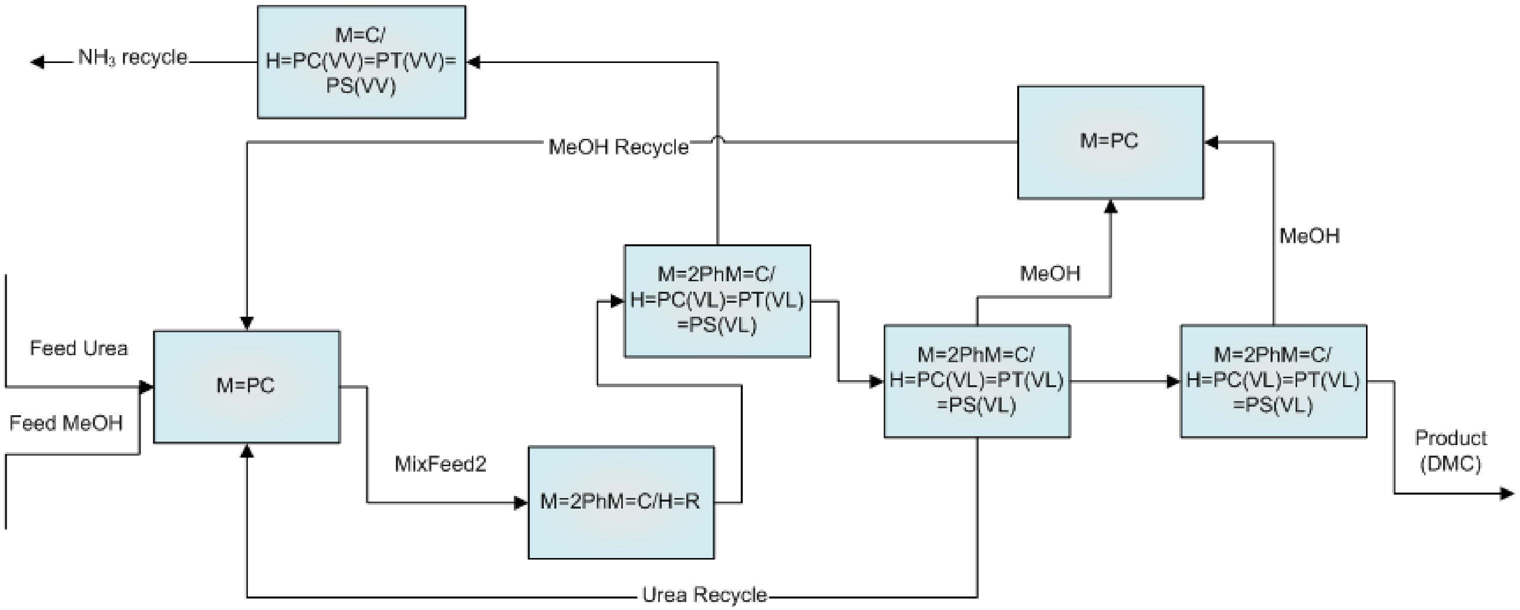


Figure 6.6 - Phenomena-based representation of the base case flowsheet for DMC production by the urea route.

Table 6.11 - Operating window for the considered phenomena in this study. (Adapted from Babi *et al*., 2015).

No	**Phenomena**	**Operating Window**
PBB. 1	*R*	T_{low}: 120˚C (Lowest melter or insufficient for activation energy) T_{high}: 170˚C (Catalyst degrade or inhibit reaction equilibrium)
PBB. 2	M_{ID} *(mixing)*	T_{low} = -98.68˚C (Lowest melter) T_{high} = 132.70˚C (Highest boiler)
PBB. 3	$M_{FL,tube}$ *(mixing)*	
PBB. 4	$M_{FL,rec}$ *(mixing)*	
PBB. 5	M_{V} *(mixing)*	
PBB. 6	*2phM (mixing)*	T_{low} = 64.70 ˚C (Lowest boiling azeotrope) T_{high} = 177.0˚C (Highest boiler)
PBB. 7	*PC(VL)* Conventional separation vapor-liquid	V-L present
PBB. 8	*PT(VV)* conventional separation vapor-vapor	Component affinity
PBB. 9	*PT(VL)*	T_{low}= 64.70 ˚C (Lowest boiling azeotrope)
PBB. 10	*PT(PVL)* Non-conventional separation vapor-liquid	T_{operate}= 70.0 ˚C (Membrane stability in pervaporation unit)
PBB. 11	*PS(VL)*	V-L Present
PBB. 12	*PS(VV)* Non-conventional separation vapor-vapor	V-V Present
PBB.13	*H*	Heating
PBB. 14	*C*	Cooling
PBB. 15	*D*	Dividing

8.3. Identification of desirable task and phenomena

According to Babi *et al*., (2014), the process hot-spots can be reduced/eliminated through the use of additional, desirable PBBs using thermodynamic insights (Jaksland *et al*., 1995). The set of PBBs are: M (considering 4 types), 2phM, H, C, R, PC(VL), PT(VL), PT(PVL), PT(VV), PS(VL), PS(VV) and D and their operating window is defined in Table 6.11. Each process hot-spot is linked to a binary ratio property (Jaksland *et al*., 1995) that translates into a (desirable) PBB (see examples in Table 6.14). For example, if the molar volume binary ratio of an azeotrope pair is greater than 1.5 (Jaksland *et al*., 1995) then the PBB PT(PVL) is selected and added to the initial set of PBBs. This PBB is the building block of a pervaporation membrane or unit operation that incorporates pervaporation at the unit operations scale. An excerpt of the binary ratio matrix for the compounds is given in Table 6.12. It can be see that for the DMC/MeOH binary pair, the radius of gyration is 2.09 and van deer Waals volume is 2.13 therefore, the following desirable PBBs are selected: PT(PVL), PT(VV) and PS(VV).

Table 6.12 - Computed binary ratio matrix for a selected set of compounds for the DMC production process

Ratio of properties of binary pairs	*Mw (g/mol)*	*Tm (K)*	*Tb (K)*	*RG (Å)*	*Solubility parameter ($MPa^{0.5}$)*	*V_{VDW} (m^3/mol)*	*V_M (m^3/mol)*	*Vapor pressure (atm)*	*Dipole moment (debye)*
DMC/MC	1.2868	0.8514	0.8072	-	-	-	-	-	-
DMC/NH_3	5.2891	1.4080	1.5159	3.8065	2.99E-01	3.3478	2.87E+00	7.38E-03	0.6120
DMC/MeOH	2.8112	1.5680	1.0756	2.0921	16372.72	2.1290	1.9664	2.3278	0.5289
MeOH/Urea	0.5335	0.4323	0.7265	0.5969	1.20E-03	0.6718	7.72E-01	6.26E+03	0.3730
MeOH/MC	0.4577	0.5429	0.7505	-	-	-	-	-	-
MeOH/NH_3	1.8813	0.8979	1.4093	1.8194	1.82E-05	1.5724	1.46E+00	3.17E-03	1.1571
Urea/MC	0.8579	1.2559	1.0329	-	-	-	-	-	-
Urea/DMC	0.6667	1.4750	1.2795	0.8007	5.10E-02	0.6991	6.59E-01	6.87E-05	5.0682
Urea/NH_3	3.5262	2.0769	1.9397	3.0480	1.52E-02	2.3405	1.89E+00	5.07E-07	3.1021

MW – molecular weight (g), Tb – normal boiling point (K), RG – radius of gyration (Å), Tm – normal melting point (K), V_M – molar volume (m^3/mol), SolPar (Hansen) solubility parameter, V_{VDW} (m^3/mol) – Van der Waal volume, V_P (atm) – vapor pressure.

Table 6.13 - List of selected (desirable) PBBs linked to the identified tasks *V*-vapor, *L*-liquid, LL- liquid-liquid, MSA-mass separating agent.

Hot-spot	Main Task	Property/Binary ratio	Alternative Task	MSA	PBB (desirable)
Azeotrope	Separation	Vapor pressure, solubility parameter	Separation	Yes	PC(LL), PT(LL), PS(LL)
Azeotrope	Separation	Radius of gyration, van deer Waals volume, solubility parameter	Separation	No	PT(PVL), PT(VV), PS(VV)
Difficult separation due to low driving force					

8.4. Generation of feasible operation/flowsheet option

A simultaneous phenomena building block (SPB) is defined as the combination of one or more phenomena building blocks using predefined combination rules (Babi *et al*., 2015) for example, SPBs containing the combination of H and C PBBs to form =H=C= are rejected because of thermodynamic infeasibility, SPBs containing the combination of R and C PBBs to form =R=C represent a liquid phase reaction coupled with cooling (Babi *et al*., 2014). The 15 identified PBBs are combined to form SPBs and the possible number of combinations based on the formula proposed by Lutze *et al*., (2013) is calculated to be 16728. Using the connectivity rules proposed by Lutze *et al*., (2013) and Babi *et al*., (2015), identification of desirable tasks to PBBs, given in Table 5.13, the number of (feasible) SPBs is reduced to 72 (see Table 6.14). Note that that when combining PBBs into SPBs, the combination of simultaneous reaction and separation is feasible (see SPB 11) which verifies the merging of reaction and separation tasks into one single task.

Table 6.14 - The partial list of identified feasible *SPBs* together with corresponding interconnection phenomena and inlet and outlet conditions.

SPB	Interconnection Phenomena	In	Out
SPB.1	*M*	1…n(L,VL,V)	1(L,VL,V)
SPB.2	*M=R*	1…n(L,VL,V)	1(L,VL,V)
SPB.3	*M=H*	1…n(L,VL,V)	1(L,VL,V)
SPB.4	*M=C*	1…n(L,VL,V)	1(L,VL,V)
SPB.5	*M=R=H*	1…n(L,VL,V)	1(L,VL,V)
SPB.6	*M=R=C*	1…n(L,VL,V)	1(L,VL,V)
SPB.7	*M=2phM*	1...n(L,VL)	1(V/L)
SPB.8	*M=R=2phM=PC(VL)=PT(VL)*	1...n(L,VL)	1(V/L)
SPB.9	*M=2phM=PC(VL)=PT(VL)=PS(VL)*	1...n(L,VL)	2(V;L)
SPB.10	*M=R=2phM=PC(VL)=PT(VL)=PS(VV)*	1...n(L,VL)	2(V;L)
SPB.11	*M=R=2phM=PC(VL)=PT(VL)=PS(VL)*	1...n(L,VL)	2(V;L)
SPB.12	*M=R=2phM=PC(VL)=PT(VV)=PS(VV)*	1...n(L,VL)	2(V;V)
SPB.13	*M=C=2phM=PC(VL)=PT(VL)*	1...n(L,VL)	1(V/L)
SPB.14	*M=H=2phM=PC(VL)=PT(VL)*	1...n(L,VL)	1(V/L)
SPB.15	*M=H=R=2phM=PC(VL)=PT(PVL)*	1...n(L,VL)	1(V/L)
SPB.16	*M=C=R=2phM=PC(VL)=PT(PVL)*	1...n(L,VL)	1(V/L)
SPB.17	*M=H=R=2phM=PC(VL)=PT(VL)=PS(PVL)*	1...n(L,VL)	2(V;L)
SPB.18	*M=H=R=2phM=PC(VL)=PT(VL)=PS(VL)*	1...n(L,VL)	2(V;L)
SPB.19	*M=H=R=2phM=PC(VV)=PT(VV)=PS(VV)*	1…n(L,VL)	2(V;V)
SPB.20	*M=2phM=PC(VL)=PT(PVL)=PS(VL)*	1...n(L,VL)	2(V;L)
SPB.21	*M=2phM=PC(VL)=PT(VL)=PS(VV)*	1...n(L,VL)	2(V;L)
SPB …	...	…	…
SPB.72	*D*	1…n(L,VL,V)	1…n(L;VL;V)

Note: *V* = vapor; *L* = liquid; “/” means “or”; “;” means “and”; “In” provides number of inlet streams (1 to n) and phase, “Out” provides number of outlet streams (1 or 2) and phase.

The process alternatives are generated from the *SPBs* listed in Table 6.14. The criteria for generating new process alternatives are given in Table 6.15. The new process alternatives are based on the reaction and raw materials defined in the base case design. MeOH (raw material) forms an azeotrope with DMC (desired product). From the constraints defined in Table 6.15, the separation involving mass separating agents (solvents) are not considered in order to minimize waste generation. From the mixture property analysis Kongpanna *et al*., (2015) MeOH/DMC has azeotrope that is also pressure dependent. For the separation of the separation of the MeOH/DMC azeotrope (and based on the desirable PBBs selected in step 8.3) SPBs consisting of PT(PVL) and PT(VV) are selected.

Table 6.15 - The details of desirable tasks and process intensification constraints

Bottlenecks	**Primary task**	**Desirable task**	**Details of desirable task: Debottleneck**
Activation problems	Reaction	Reaction	a. explore new reaction pathways = NO
			b. Explore new catalysts = NO
		Mixing/Heating	a. The reactor operate at 170 °C and 20 bar, and feed stream have to heat up before flow to reactor
Azeotrope	Reaction i. In a reactor effluent after reaction ii. In a stream where the product/component to be recovered has formed an azeotrope with another component	Reaction	a. An additional reaction task is added to react away one of the component that form azeotrope
			b. Constraint 1: If an additional reaction is added, the reaction must not react with the product or unreacted raw material
			c. Constraint 2: If the reaction involves unreacted raw material, the product produced from this reaction must be valuable and can be sold when recovered
			Explore new type of the reactor design which allow the removal of one of the components which is part of the azeotrope (Figure 4.7.)

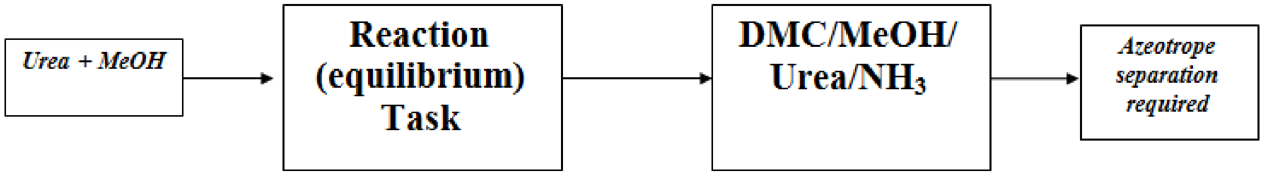


Figure 6.7 - Existing process with requirement on azeotropic separation

		Stream (After reaction section) There are some researches reporting uses of Pervaporation, Catalyst as absorption and so on.	a. Solvent based separation task: Extractive separation Liquid-Liquid separation Absorption separation Stripping ==== NO due to waste minimization ====
			b. Size separation
			c. Permeability/Affinity separation
Contact problem of raw materials/limited mass transfer	-	-	-
Degradation by temperature	-	-	-
Difficult separation due to	-	-	-

low driving force			
Explosive mixture	-	-	-
Formation of undesired side-products	-	-	-
High energy consumption/ demand	Reaction	Reaction	a. Preheating raw materials before flow into reaction section b. If a homogeneous catalyst is used explore the use of solid catalyst because this means that an additional separation task is needed to recover the catalyst ==== This is considered ==== c. increase conversion of reaction for decrease amount of excessive raw material for recycle
	Separation	Separation	a. Solvent based separation task: Extractive separation Liquid-Liquid separation Absorption separation Stripping ==== NO due to waste minimization ====
			b. Improve separation system
			d. Insert new separation system
Highly endothermic reaction	Reaction	Reaction	a. explore new reaction pathways = NO
			b. Explore new catalysts = NO

		Cooling	a. This reaction is endothermic
		Heating	a. A heating medium can be placed around the reactor to maintain certain temperature b. Heating coils can be placed within the reactor to maintain a certain temperature c. the feed temperature can be increased d. The recycling of raw materials to the reactor can be cooled at a temperature comparable to point c in order to provide additional heating Preheating raw materials before flowing into reaction section. the higher temperature chosen should not inhibit the rate of reaction
Limiting heat transfer	-	-	-
Limiting equilibrium	Reaction	Reaction	a. Explore new reaction pathways = NO
			b. Explore new catalysts = NO
		Separation	a. This is considered because it may assist in generating new reactor/separation design concepts
			b. Separation and recycle of raw materials to the reactor for increase conversion

==== This is considered (Figure 4.8)====

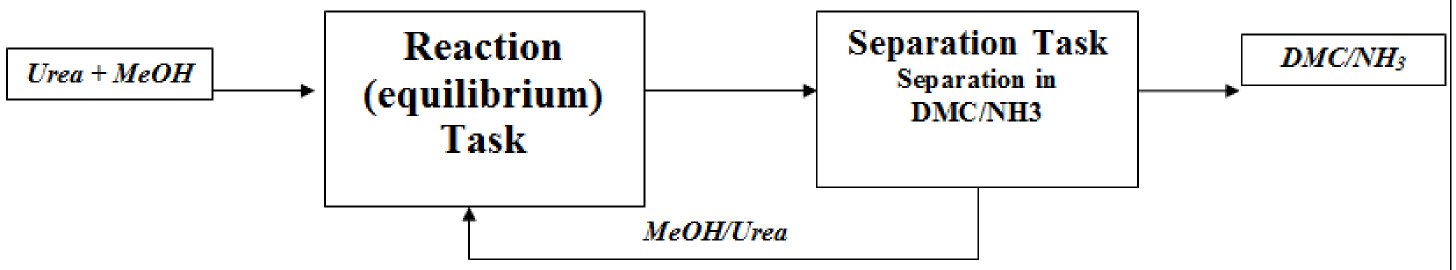


Figure 6.8 - Desirable task for process bottleneck of limiting equilibrium

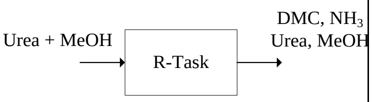
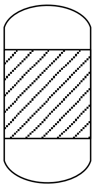
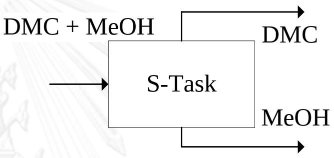
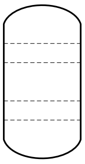
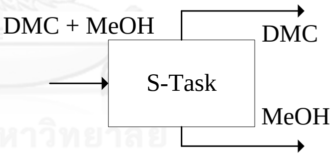
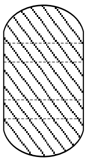
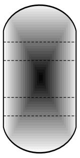
The following flowsheet alternatives are considered for the DMC synthesis section (red dotted box in Figure 6.4):

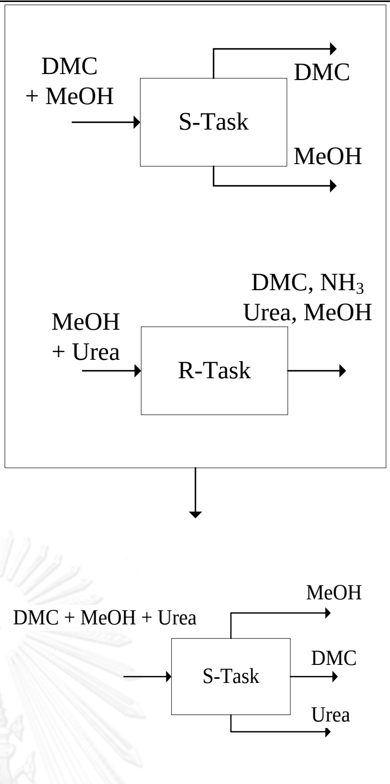
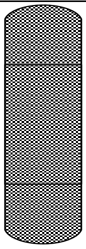
- Flowsheet alternatives 1-2 - Pervaporation or vapor-permeation membrane unit for the separation of DMC/MeOH
- Flowsheet alternative 3 - Membrane reactor reaction and *in situ* product removal for shifting the reaction equilibrium
- Flowsheet alternative 4 - Reactive distillation and membrane reactor where simultaneous reaction and product separation is performed.

These flowsheet alternatives (flowsheet alternatives 1-4) are generated using the following SPBs and further explained in Table 6.16:

- The pervaporation and vapor permeation membrane for separation of the DMC/MeOH azeotrope: SPB. 20 *(M=2phM=PC(VL)=PT(PVL)=PS(VL))* and SPB. 21 *M=2phM=PC(VL)=PT(VL)=PS(VV).*
- Membrane reactor and Reactive distillation for simultaneous reaction and separation: SPB. 17 *(M=H=R=2phM=PC(VL)=PT(VL)=PS(PVL))* and SPB. 18 *(M=H=R=2phM=PC(VL)=PT(VL)=PS(VL))*

Table 6. 16 - Generation of hybrid/intensified unit operations from combination of PBBs.

SPB No.	Combined SPBs (Basic Structure)	Task Performed	Unit operations
SPB. 5	*M=R=H*		Conventional Reactor
SPB. 7 SPB. 9 SPB. 4 SPB. 12	*M=2phM* *M=2phM=PC(VL)=PT(VL)=PS(VL)* *M=C* *M=R=2phM=PC(VL)=PT(VV)=PS(VV)*		Conventional distillation column
SPB. 20	*M=2phM=PC(VL)=PT(PVL)=PS(VL)*		Pervaporation membrane unit Vapor permeation membrane unit
SPB. 13 SPB. 8 SPB. 9 SPB.	*M=C=2phM=PC(VL)=PT(VL)* *M=R=2phM=PC(VL)=PT(VL)* *M=2phM=PC(VL)=PT(VL)=PS(VL)* *M=H=2phM=PC(VL)=PT(VL)*		

14		 *Task are merged*	 Reactive distillation Membrane reactor

The generated flowsheet alternatives are shown in Figures. 6.9-6.11. Figure 6.9 shows flowsheet alternatives 1 and 2 where a pervaporation and vapor permeation membrane are used for the separation of the DMC/MeOH (azeotrope forming) mixture. Figures 6.10-6.11 show flowsheet alternatives 3 and 4 where a membrane reactor and reactive distillation are used for *in situ* reaction and separation.

8.5. Screening of flowsheet alternatives

From the generation of feasible operation/flowsheet option, the 4 process alternatives are generated. From the 4 generated alternatives only one is screened out, the vapor-permeation membrane for downstream separation of DMC/MeOH azeotrope (process alternative 2) which have SPB. 21 M=2phM=PC(VL)=PT(VL)=PS(VV) as a phenomena building blocks. This process alternative was screened out due to insufficient data.

In order to check feasibility of the proposed three intensified process alternatives for the production of DMC they are first simulated with Aspen Plus®. The steady state process simulation has been performed. The liquid activity calculation, the UNIQUAC model has been reported by Holtbruegge *et al.*, (2013). For the reactor, the equilibrium model and RADFRAC model for reactive distillation column have been employed for obtain mass flow rate and energy consumption. For distillation columns, the RADFRAC model has been used. The details of the all process alternatives used are given in the corresponding simulation results.

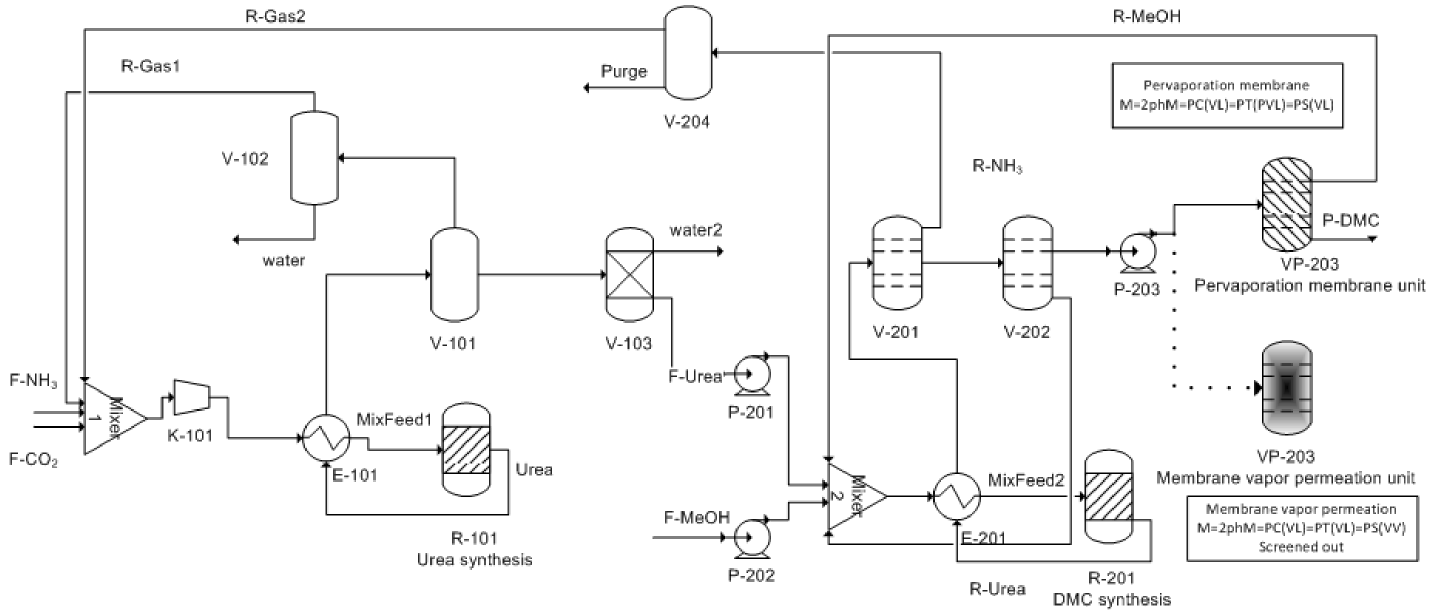


Figure 6.9 - DMC production process by urea route - process alternative 1 using pervaporation unit (VP-203) in downstream separation

The first process intensification concept for use as the process alternatives shown in Figure 6.9 is pervaporation system taken from literatures using crosslinked poly(vinyl alcohol) (PVA) membranes and poly(acrylic acid)/poly(vinyl alcohol) blended membranes (Wang *et al.*, 2007, 2009). The results reveal that the use of crosslinked PVA membrane could achieve high concentration of MeOH of 98.6wt.% in the permeate side from the feed mixture containing 40–70wt.% MeOH at 50–70 ˚C. Therefore, the pervaporation (VP-203) is set for the separation of DMC/MeOH azeotrope mixture instead of using the conventional pressurized distillation column (V-203) in the base case for reducing energy consumption which can refer to the less amount of methanol flowrate. The azeotropic mixture is moved from the distillate stream of V-202 to the pervaporation unit with a flowrate of 8434 kg/h. The pressure at the upstream side and the downstream side in the pervaporation unit was maintained at about 2 bar and 0.2 bar, respectively. According to the simulation, the flow of methanol on the permeate side is 2057 kg/h which is recycled to the separation section. The remaining of methanol is 29.21 kg/h in the product stream and DMC achieved as the product is 6072 kg/h (67.41 kmol/h) with 99.50 wt.% purity of DMC.

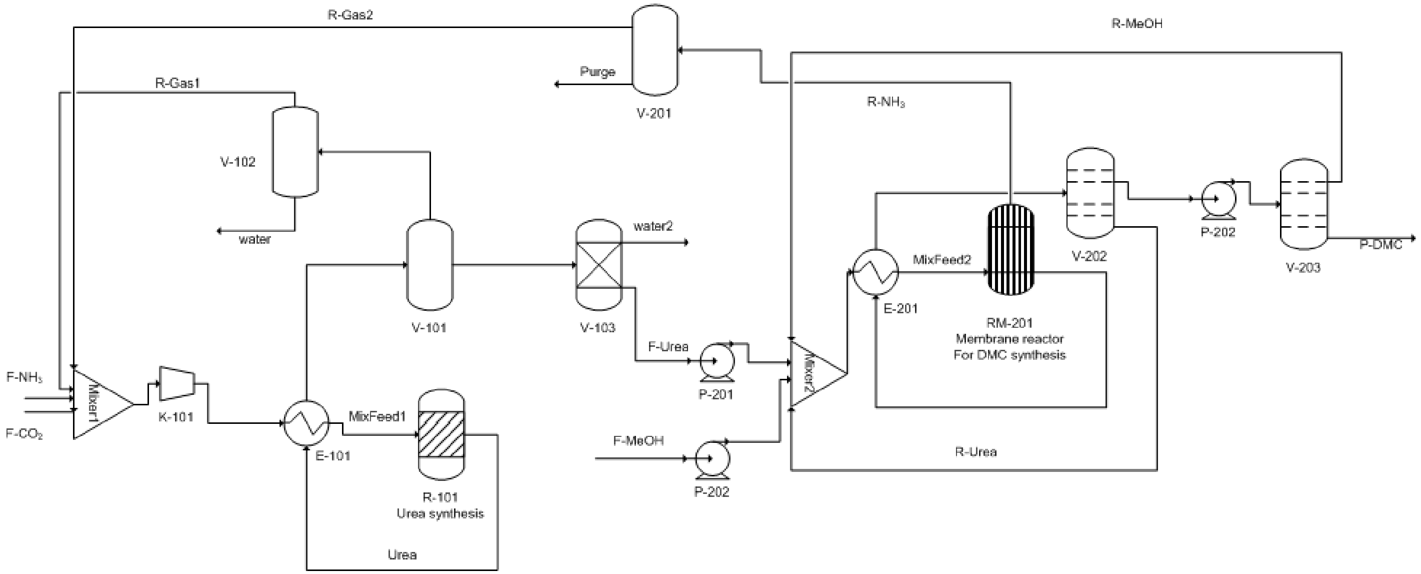


Figure 6.10 - DMC production process by urea route - process alternative 2 using membrane reactor (RM-201) for NH_3 removal.

The next alternative for process intensification shown in Figure 6.10 focuses on DMC synthesis reactor. The use of a catalytic reactor (RM-201) that can draw by-product (i.e., NH_3) out of the reactor to shift the reaction equilibrium (Wang *et al*., 2007) can significantly increase DMC yield. The reaction occurs at 12 bar 185 ˚C with a MeOH: Urea feed molar ratio of 2.6: 1 and a reflux ratio of 2. The simulation results show that this catalytic reactor offers DMC yield of 80%. The product stream was sent to the separation and purification section to achieve 5924 kg/h (65.76 kmol/h) with 99.78 wt.% purity of DMC.

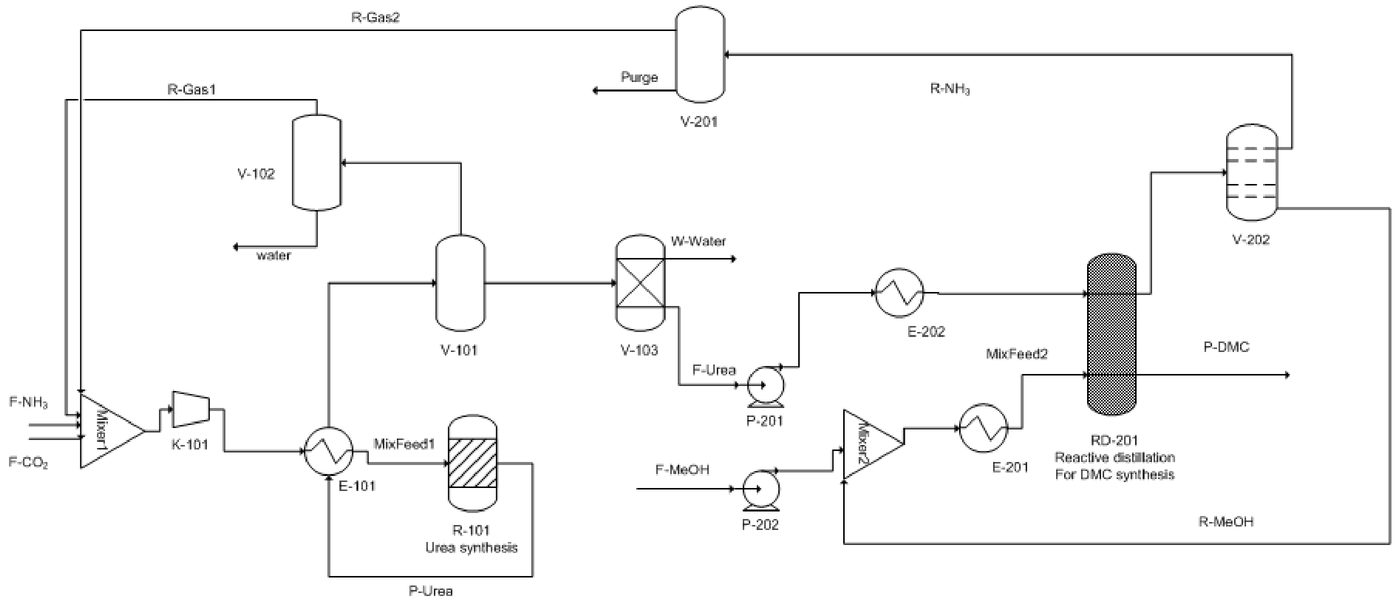


Figure 6.11 - DMC production process by urea route - process alternative 3 using reactive distillation (RD-201) for integrating reaction and separation system

The third alternative process shown in Figure 6.11 focuses on integration of reaction and separation together for reduce the number of unit operations, while the yield of DMC and energy efficiency are increased. Reactive distillation is used in this alternative (Wang *et al*., 2012). The feed streams contain 4565 kg/h of urea and 5126 kg/h of MeOH plus with the recycled MeOH from downstream separation at the molar ratio of urea: MeOH of 2:1. The reactive distillation (RD-201) has 40 stages, whereas the reaction zone is stage 17-36. Urea is fed at stage 16 and MeOH is fed at stage 26. The distillate stream, which contains NH_3, urea, MeOH and DMC is sent to the flash separator to separate and recycle NH_3 to the urea synthesis section, the unreacted urea, MeOH and some DMC product would be recycled and sent to the reaction section. For the DMC product which is the bottom stream of DMC synthesis reactor has the production rate of 6157 kg/h (68.35 kmol/h). This process results in very high yield of DMC (97.5%) and high purity of DMC in the product 99.7 wt.%.

More studies for DMC production from CO_2 utilization have been carried out to compare the DMC production by the urea route with the other process candidates, including: 1) the EC process and 2) the intensified EC process by using reactive distillation (Hsu *et al*., 2010) as the DMC synthesis reactor and 3) conventional BAYER process by partial carbonylation reaction of carbon monoxide (CO) process (Kricsfalussy *et al*., 1996), the process data and process flowsheets are given in Figures 6.12, 6.13 and 6.14, respectively.

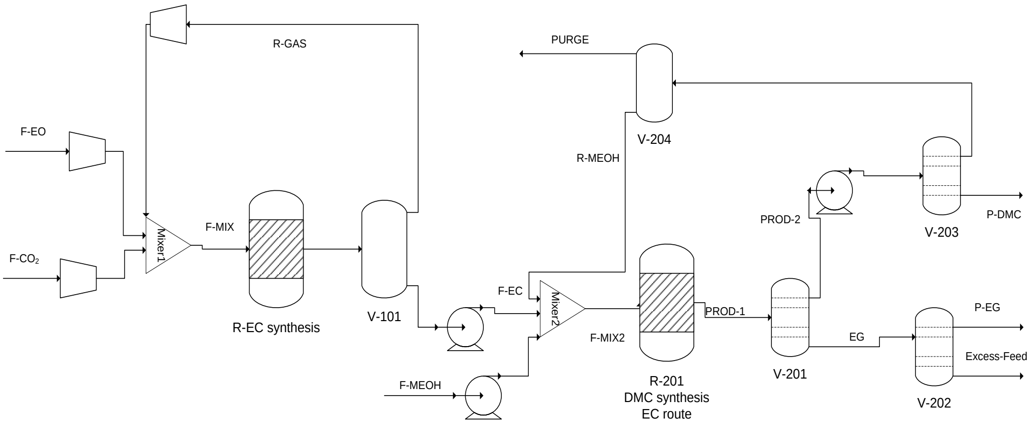


Figure 6.12 - DMC production process by ethylene carbonate route using conventional reactor.

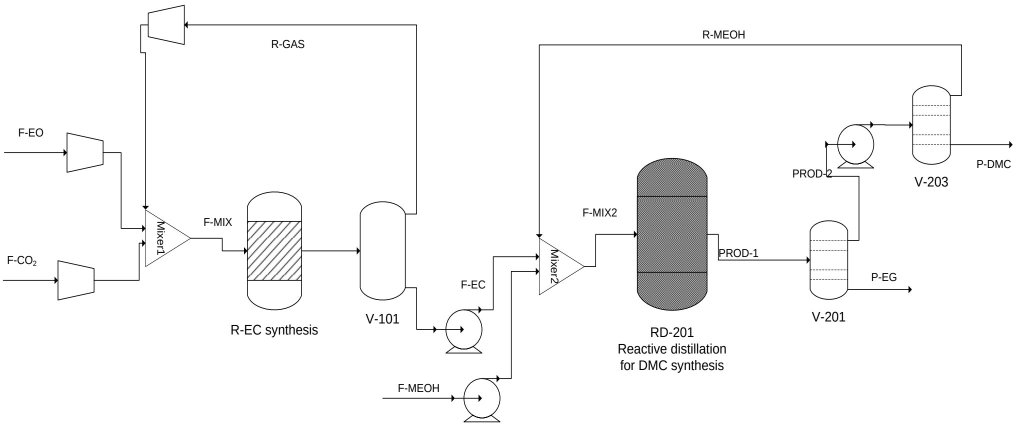


Figure 6.13 - DMC production process by intensified ethylene carbonate route using reactive distillation (RD-201)

BAYER process

The simulation of the BAYER process is based on the information provided in the patent (Kricsfalussy *et al*., 1996). The process flow diagram is shown in Figure 6.14. The UNIQUAC model (Gmehling *et al*., 2012) is used for the vapor-liquid equilibrium calculations. The partial carbonylation reaction of CO and MeOH is carried out in a reactive-distillation unit (Mohamed *et al*., 2007, Simasatitkul *et al*., 2013). Here, a gas-phase exothermic reaction is taking place where the excess reactant is removed, the equilibrium conversion shifted and azeotrope formations are avoided. The reaction temperature is known to vary between 120 ˚C to 300 ˚C, but values between 120 ˚C to 180 ˚C are preferred. The reaction is carried out at atmospheric pressure. However, to achieve a sufficiently high reaction rate, it is advantageous to carry out the reaction at a higher pressure, preferably between 10 to 50 bar, with the optimal between 12-22 bar. Water, which is formed from the reaction, is removed from the system, optionally after distilling off organics such as the DMC. In the zone of the reactive-distillation unit, molten salts, methanol and DMC are distilled off, together with small amounts of volatile by-products such as, formaldehyde and dimethyl acetal.

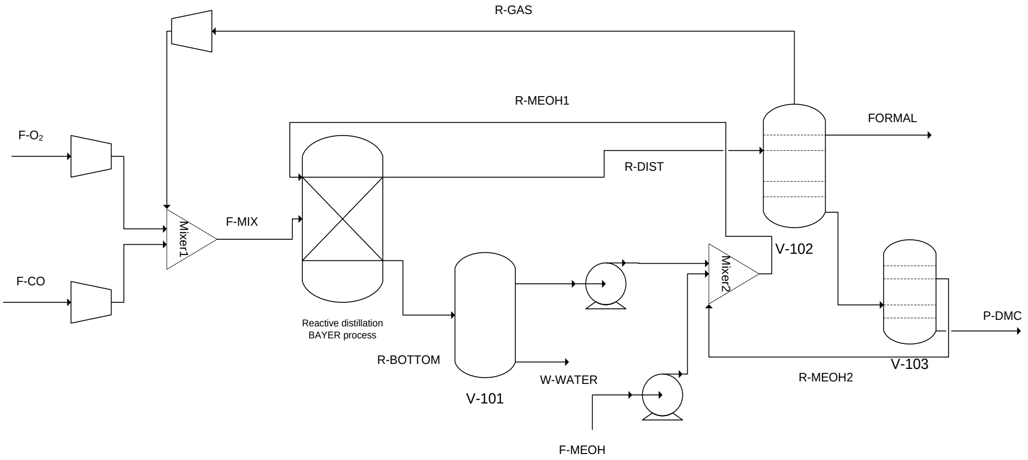


Figure 6.14 - DMC production process by BAYER.

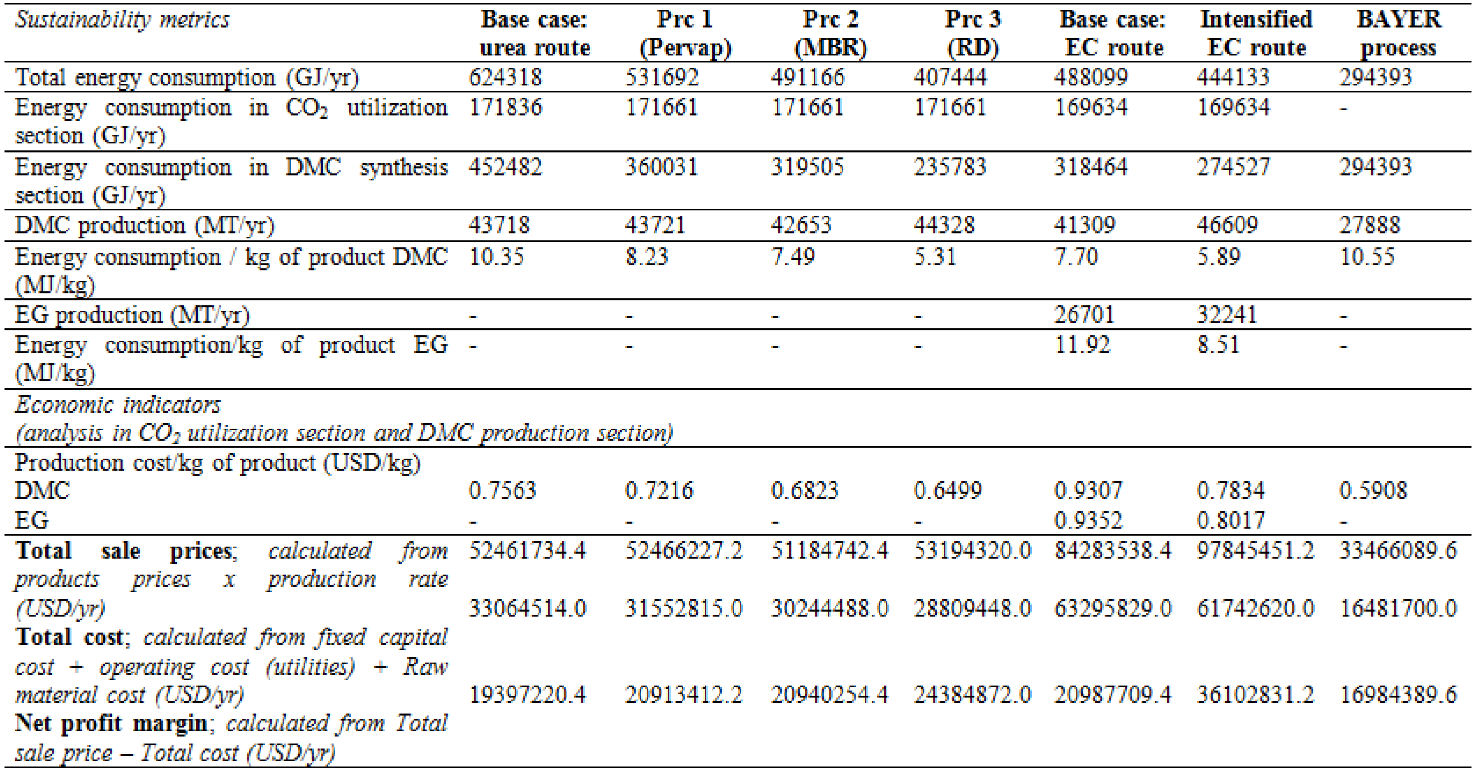
Methanol introduced into the reaction zone contains relatively large amounts of DMC which, for example, has a composition corresponding to the MeOH/DMC azeotrope. It is possible to obtain a higher yield of DMC by shifting the equilibrium through the addition of excess MeOH. The BAYER process has also been simulated through Aspen Plus$^{®}$ using the reported design (Kricsfalussy *et al*., 1996). The simulation results are agree well with those reported in the patent, in terms of DMC yield of 99.5% and the process stream compositions.

8.6. Evaluation of feasible flowsheet alternatives

Here, the performances of the generated alternatives are compared in terms of sustainability selected metrics, economic factors and life cycle assessment factors as summarized in Table 6.17. The product purity is 99% weight or higher for DMC. Energy consumption which are obtained from the process simulator are considered in term of energy usage per one unit of product as sustainability selected metrics, fixed capital investment cost and operating cost, HTC and GWP, CO_2 emission considered in term of CO_2 emission per one unit of product, are considered. The three process alternatives obviously offer superior performance in terms of all indicators to the base case process. The best process alternative is the reactive distillation option (Process alternative 3). The energy consumption per one unit of DMC is significantly reduced (51.28%) as well as the fixed-capital cost (54.61%) and the operating cost (61.14%). The cold utilities (cooling water) and hot utilities (steam) usage were reduced to 41.63% and 52%, respectively. In addition, the CO_2 footprint, HTC and GWP were reduced to 19.59%, 80.00% and 59.49%, respectively. In addition, more studies of DMC production have been carried out to compare the DMC production by the urea route with the other process candidates, including: 1) the EC process and 2) the intensified EC process by using reactive distillation (Hsu *et al.*, 2010) as the DMC synthesis reactor and 3) conventional BAYER process by partial carbonylation reaction of carbon monoxide (CO) process (Kricsfalussy *et al.*, 1996) as shown in previous section will be compare with the optimal case from this method.

The results indicate that among the CO_2-based processes, the intensified-urea route for DMC production still shows the best performance in terms of sustainability, economic, life cycle assessment due to the lower raw material cost, less CO_2 emission per unit of product and avoidance of hazardous materials usage such as ethylene oxide from EC route and carbon monoxide from BAYER process. Moreover, the DMC production by the intensified option of urea route and the EC route indicate the competitive prices when compared to the BAYER process. Because for the urea route, the cost of production is quite small (0.6499 USD/kg) when compared to the BAYER process (0.5908 USD/kg) and for the EC route, EG is also produced as a valuable by-product but has the higher cost of raw materials (0.9307 USD/kg for EC route base case and 0.7834 USD/kg for intensified EC route). It should be noted that process alternatives cannot be guaranteed unless all the possible alternatives are generated at the phenomena level and then screened to find the optimal solution. In this work only the DMC production by urea route and urea process alternatives are represented in Figure 6.15. In this work, although only the reaction for DMC synthesis and the adjacent separations were targeted for intensification, it can be claimed that a more sustainable alternative is achieved.

Table 6.17 - Comparison of the base case design of urea route with generated alternative process flowsheets, ethylene carbonate route, BAYER as conventional processing route and the alternatives with process intensification concept.



Sustainability metrics	**Base case: urea route**	**Prc 1 (Pervap)**	**Prc 2 (MBR)**	**Prc 3 (RD)**	**Base case: EC route**	**Intensified EC route**	**BAYER process**
Total energy consumption (GJ/yr)	624318	531692	491166	407444	488099	444133	294393
Energy consumption in CO_2 utilization section (GJ/yr)	171836	171661	171661	171661	169634	169634	-
Energy consumption in DMC synthesis section (GJ/yr)	452482	360031	319505	235783	318464	274527	294393
DMC production (MT/yr)	43718	43721	42653	44328	41309	46609	27888
Energy consumption / kg of product DMC (MJ/kg)	10.35	8.23	7.49	5.31	7.70	5.89	10.55
EG production (MT/yr)	-	-	-	-	26701	32241	-
Energy consumption/kg of product EG (MJ/kg)	-	-	-	-	11.92	8.51	-
Economic indicators *(analysis in CO_2 utilization section and DMC production section)*							
Production cost/kg of product (USD/kg)							
DMC	0.7563	0.7216	0.6823	0.6499	0.9307	0.7834	0.5908
EG	-	-	-	-	0.9352	0.8017	-
Total sale prices; *calculated from products prices x production rate (USD/yr)*	52461734.4	52466227.2	51184742.4	53194320.0	84283538.4	97845451.2	33466089.6
Total cost; *calculated from fixed capital cost + operating cost (utilities) + Raw material cost (USD/yr)*	33064514.0	31552815.0	30244488.0	28809448.0	63295829.0	61742620.0	16481700.0
Net profit margin; *calculated from Total sale price – Total cost (USD/yr)*	19397220.4	20913412.2	20940254.4	24384872.0	20987709.4	36102831.2	16984389.6

Profit (USD/kg)	0.4437	0.4784	0.5177	0.5501	0.2693	0.4166	0.6092
Product DMC	-	-	-	-	0.3648	0.4983	-
Product EG							
Fixed-capital Investment (USD/yr)	7163341	5929793	4984436	3911958	5437436	3955566	2708148
Operating cost (USD/yr)	632053	606592	496314	386444	517023	445684	298061
Raw material cost (USD/yr)	25269120	25016430	24763738	24511046	57341370	57341370	13475491
Cooling water usage (GJ/yr)	194954.4	116424.0	118958.4	81172.8	132602.4	121910.4	98496
Fuel usage (GJ/yr)	295783.2	243187.2	177696.0	153813.6	285235.2	284104.8	175824
CO_2 usage in process as raw material (MT/yr)	24732.0	24732.0	24732.0	24732.0	24411.6	24411.6	-
Life cycle assessment indicator							
CO_2 emission from process (MT/yr)	80769.87	53942.57	46933.38	35867.34	41484.72	41936.82	14557.74
CO_2 reduction by utilization (MT/yr)	24732.0	24732.0	24732.0	24732.0	24411.6	24411.6	-
Net CO_2 reduction; calculated from CO_2 emission from process – CO_2 reduction by utilization (MT/yr)	56037.87	29210.57	22201.38	11135.34	17073.12	17525.22	14557.74
CO_2 emission kg / kg of product DMC	1.2818	0.6681	0.5205	0.2512	0.4133	0.3760	0.5220
HTC / kg of product DMC	0.000306	0.000268	0.000251	0.000245	0.000454	0.000362	0.000493
GWP / kg of product DMC	3.5528	2.8504	2.6626	2.1138	4.2048	2.4448	1.808

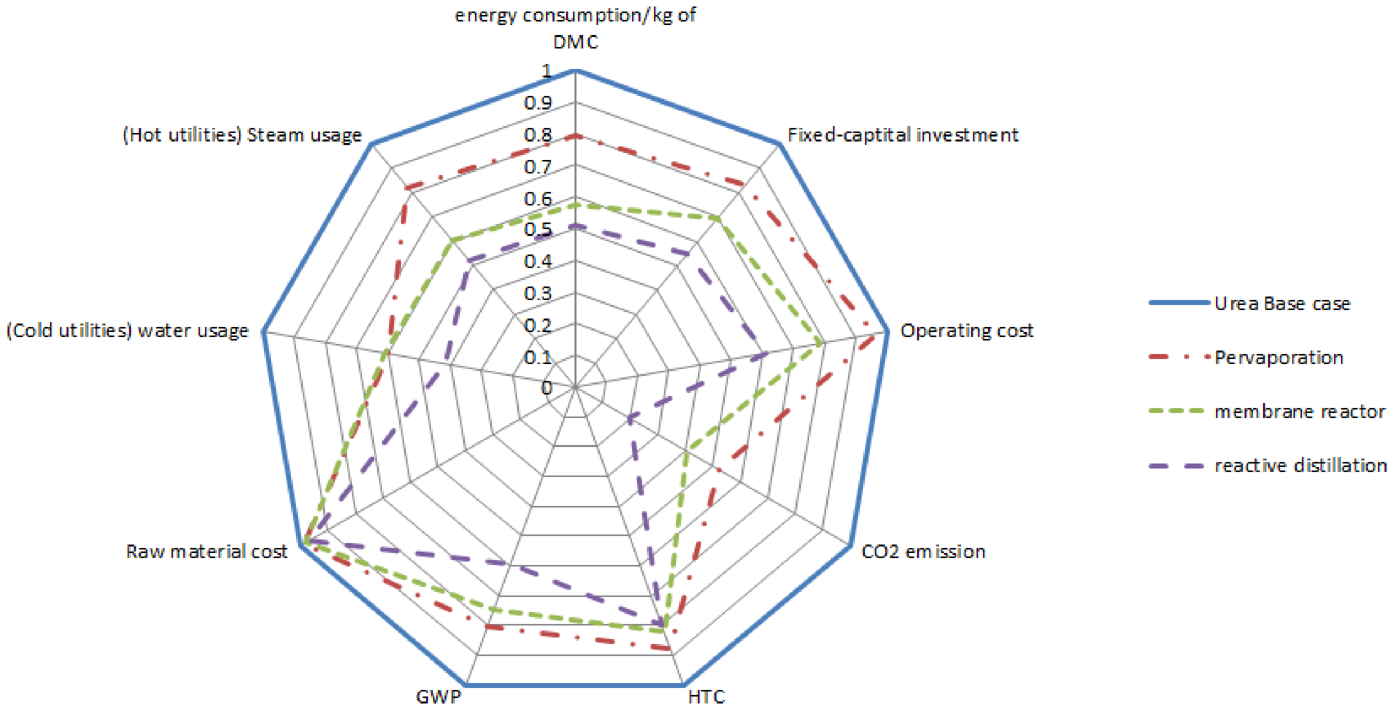


Figure 6.15 - Process performance evaluation of the process alternatives compared to the base case design.

CHAPTER VII
CONCLUSION & RECOMMENDATION

7.1 Conclusion

The main contribution of this thesis is on development of the framework for process synthesis-design-intensification where the three-stages decomposition approach has been implemented together with the associated work-flow and data-flow. The investigation on DMC production by CO_2-based process integrated computer aided tools with the systematic approach solution has developed. The decomposition based approach of process synthesis-design and process intensification has been implemented into a systematic framework, which has been applied to a CO_2-based utilization process. All applications of all three stages: network synthesis, base case design and identification of innovative more sustainable process alternatives have been highlighted through the application example (DMC production case study). A superstructure of processing routes has been generated and evaluated to determine the most promising processing route, which was then analyzed in detail to identify design improvement targets. Through a phenomena-based method, new more sustainable process alternatives matching the design improvement targets have been identified. For the evaluation of alternatives, the measures used in this thesis, include the global important issues, environmental and economic measures, the performance criteria also considers measures for more sustainable alternatives, such as, energy consumption, net CO_2 emission, raw material depletion and life cycle assessment factors at their targeted levels or better. It was found that the alternative options which were generated through the phenomena based synthesis method, are better than the base case design. As developed, the framework is generic and can be applied to any chemical or biochemical processes and current work involves the application of it to determination of sustainable biorefinery solutions as well as sustainable wastewater treatment networks and a more comprehensive CO_2-utilization based processes covering more than one product.

In this thesis, the proposed systematic methodology was applied to the CO_2-based DMC production processes. A superstructure of processing routes including CO_2 direct synthesis and indirect syntheses via urea, ethylene carbonate and propylene carbonate, was generated and evaluated to determine the most promising processing route, DMC production by urea route was obtained as base case design. The process analysis indicted the energy waste cost in reaction section and downstream separation section of DMC production as the process "hot-spots" which were identified as design improvement targets. Then the process intensification: A phenomena-based method was used to generate more sustainable process alternatives. The feasible flowsheet alternatives have been generated, pervaporation membrane, membrane reactor and reactive distillation, including those containing hybrid/intensified unit operations. These have been generated using a rule based approach by first combining PBBs to form SPBs. These SPBs are then combined to form basic structures that satisfy a task or set of tasks for reaction, separation and, simultaneous reaction and separation. The evaluation of alternatives, the measures include sustainability metrics, economic potential indicators as well as LCA factors. The intensified-urea route for DMC production by reactive distillation shows the best performance in terms of sustainability, economic, life cycle assessment, less CO_2 emission per unit of product and avoidance of hazardous materials, offering superior performance to the conventional BAYER process.

7.2 Recommendation

For the DMC production, the direct synthesis of DMC by CO_2 and methanol was recently reported as a favorable technology (in 2015 from Twente University). In their process, methanol and CO_2 reacted to DMC in a reactor, offering a conversion of 92.4%. The unreacted species were separated from the stream and recycled back to the reactor in multiple steps. The reacted dehydrating agent was regenerated and recycled with the unreacted agent to the reactor. The CO_2 was recycled with little pressure drop and the dehydrating agent was separated by distillation. Finally, the methanol/DMC azeotrope was broken by using an extractive distillation with phenol as a solvent. The study did not consider regeneration of solvent in downstream separation. The investment cost was \$33 million and the process was estimated to yield a profit of \$57 million per year. The regeneration section was not included. A sensitivity analysis was made to estimate the impact of the regeneration section. A maximum loss of 1.4% of the 2-cyanopyridine was allowable. Significant investment is possible in the regeneration section, while remaining profitable. To conclude; regeneration needs further investigation.

In our work, the DMC from the intensified urea route with the reactive distillation was estimated to sale price of \$53.1 million per year and indicated the high investment, utility and operating cost which was estimated at \$28.8 million per year, yielding a profit of \$24.3 million per year. Our proposed process indicated the lower profit than the newest process proposed by Twente University, due to the starting raw material cost (NH_3), the capital investment cost and operating cost in urea synthesis reaction and separation section which are required for producing urea as chemical intermediate for the DMC production. However, the direct synthesis of DMC from CO_2 and MeOH from Twente University was not included the part of regeneration process which requireed phenol as a solvent, energy for regeneration this amount of phenol and life cycle assessment indicators (waste minimization algorithm). Nevertheless, the direct synthesis of DMC from CO_2 and methanol are very interesting with further innovation and process intensification concept.

The systematic framework can be applied to any chemical processes. To achieve the higher level of more sustainable process design, the process synthesis and design must be intense at the first step. Nevertheless, the process can be retrofitted by using process analysis and use process intensification concept.

There are high demands of researches on CO_2 utilization, such as CO_2 to methanol, CO_2 to salicylic acid and other fine chemicals which still require the engineering knowledge. Process simulation, validation, optimization and intensification are the important keys to achieve more sustainable process design for CO_2 utilization.

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APPENDICES

APPENDIX

Content;

1. Superstructure generation code for CO_2 utilization network.
2. Process simulations of DMC production by urea route.
3. Additional data for all simulation processes of the urea route.
4. Process simulations of DMC production by the EC route.
5. Economic evaluation of the processes (include verification with Plant design and economic for chemical engineer book, Timmerhaus, 1991).

1. The generic code for using in GAMS (superstructure generation).

```
        * Generate Binary File and download


$onecho >input.txt
        Set=i           rng=components!                rdim=1
        Set=kk          rng=Intervals!A2:A201          rdim=1
        Set=react       rng=theta!A1:A10               rdim=1
        Set=rr          rng=reactions!                 rdim=1
        Set=j           rng=Fpoints!A1:A200            rdim=1
        Set=step        rng=Intervals!B1:BB1           cdim=1
        par=muc         rng=muc!                       rdim=2 cdim=1
        par=MW          rng=mw!                        rdim=1
        par=PHI         rng=phi!                       rdim=1 cdim=1
        par=S           rng=S!                         rdim=1 cdim=1
        par=SP          rng=SP!                        rdim=1 cdim=1
        par=PS          rng=Intervals!                 rdim=1 cdim=1
        par=SW          rng=SW!                        rdim=1 cdim=1
        par=alpha       rng=alpha!                     rdim=1 cdim=1
        par=Split       rng=Split!                     rdim=1 cdim=1
        par=gamma       rng=gamma!                     rdim=2 cdim=1
        par=theta       rng=theta!                     rdim=2 cdim=1
        par=P1          rng=P1!A1:B20                  rdim=1

        par=P2          rng=P2!A1:B20                  rdim=1
        par=P3          rng=P3!A1:B20                  rdim=1
        par=dist        rng=distance!                  rdim=1 cdim=1
        par=wasteCost   rng=scalars!B1:B1              rdim=0 cdim=0
        par=NS          rng=scalars!B2:B2              rdim=0 cdim=0

        par=NRAW        rng=scalars!B3:B3              rdim=0 cdim=0
```

```
par=NPROC       rng=scalars!B4:B4           rdim=0 cdim=0
par=Fpoint      rng=Fpoints!A1:B200            rdim=1
par=AlphaLin    rng=AlphaLin!               rdim=1 cdim=1
par=BetaLin     rng=BetaLin!                rdim=1 cdim=1
$offecho
$CALL GDXXRW.EXE NBPinput_NEW.xlsx @input.txt
$GDXIN NBPinput_NEW.gdx    # Open the Binary File

*       SETS Definition
SETS    i (*) component list
        kk(*) intervals
        react(i) reactants
        rr(*) reactions
        p  power    / Ac,Nc /
        j(*) flow points
        step(*) process step

        alias(k,kk)
        alias(i,ii)   ;
$LOAD i kk react j rr step

*       Define the parameters
Scalar          M /10000/; # Large number (used for big-M notation)
Parameters
        NS                      Number of Monte Carlo Samples
        MW(i)                   Molecular weight of component i
        PHI(i,kk)               Composition of the feed
        dist(k,kk)              transportation distance
        TrPrice                 Transportation Price (USD km MT) /0.1/
        S(k,kk)                 superstructure
        SP(k,kk)                Superstructure of primary outlet
```

```
        PS(kk,step)             Allocation of process interval to the different
steps
        epsilon(i,k,kk)         split
        SW(i,kk)                waste fraction
        alpha(i,kk)             ratio of chemical consume in the reaction
        muc(i,ii,kk)            ratio of chemical added
        Split(i,kk)             Split factor
        P1(kk)                  dollar price per feedstock per mass
        P2(i)                   dollar price of chemical per MT
        P3(kk)                  dollar price of Products per kg
        P4(p,kk)                parameters for capital investment
        gamma(i,kk,rr)          stoichiometric coefficient of products in reaction
        theta(react,kk,rr)      fraction conversion of the reactant
        NRAW                    number of Raw Materials
        NPROC                   number of Processing Units
        WasteCost               Generic cost of wastes (USD MT)
        Fpoint(j)               Flow points for piecewise linearization
        AlphaLin(j,kk)          Coefficients for Capital piecewise linearization
#
        BetaLin(j,kk)           Coefficients for Capital piecewise linearization
;

*       Reads the parameter value from the binary file
$LOAD muc MW PHI P1 S SW alpha P2 P3 dist Split SP gamma theta
NRAW NPROC WasteCost Fpoint AlphaLin BetaLin PS
$GDXIN    # Close the binary file
display i, kk, react, j, rr, step, muc, MW, PHI, P1, S, SW, alpha, P2, P3, dist,
Split, SP, gamma, theta, NRAW, NPROC, WasteCost, Fpoint, AlphaLin,
BetaLin, PS;
*       Variable declaration
Binary variable
```

```
y(k)                    1 if the selected process k is selected or 0
otherwise
Piece(j,kk)     ;
positive VARIABLES
F(i,k,kk)               Inflow of component i to process kk coming
from k
ff(i,k)                 Mass flow after the mixing point
ffbar(i,k)              Mass flow after the reaction
ffdbar(i,k)             Mass flow outside
Fin(i,kk)               Component mass flow in a interval
Ftr(kk)                 Mass flow in interval kk (used for capital
calculation)
Fout1(i,kk)             Mass flow primary outlet
Fout2(i,kk)             Mass flow secondaty outlet
F1(i,k,kk)
F2(i,k,kk)
R(i,kk)                 Chemical use in interval kk
waste                   Amount of waste produced
sales                   Total Revenues
CTr(k,kk)               Cost for transportation from interval k to kk
TransCost               Total Transportation costs
rawcost                 Cost for Raw material   [$]
utilcost                Cost for utilities     [$]
heatcost                Cost for heating       [$]
Inv(kk)                 Capital cost for equipment
Capex                   Capital cost
WastePenal              Penalty for waste production

Fpiece(j,kk)
Invl(kk)
;
VARIABLES
```

```
Z               Objective function
;
*y.fx('11')=1;
*piece.fx('p11',kk)=0;
*execute_loadpoint 'ConceptualOut2.gdx';            # Load the solution from
Conceptual 1 to have a good variable initialization

EQUATIONS
* LOGICAL CONSTRAINTS
EL                                  # No Stream Split
EFeed234
EFeed2345
EFeedC
*EFeedN2
*EFeedEO
*EFeedPO



EAc1(i,kk), EAc2(i,kk), EAc3(kk), EAc4(kk)          # Activation Constraints
(big-M)
EFl1,EFl2,EFl3,EFl4



* PROCESS INTERVAL MODEL
Ein1(i,k,kk), EIn2(i,k), EIn3(i,kk),EIn4(kk)      # Mixing
EUt1(i,kk), EUt2(i,kk)                  # Mixing with utility
ERe(i,kk)                                 # Reaction
EOu(i,kk), EOu2                         # Waste
Eout1, Eout2                            # Separation

*RAW MATERIALS ASSIGNMENT
EFe(i,kk)                               # Raw Materials
```

```
* OBJECTIVE
CostTrans(k,kk)
*,EobCap(kk),
EobCapTot
EObSales,EObRaw,EObUtil,EObTr, EObWaste
OBJ                                  # Objective Function

EobCapInv(kk)
EobCapLflow(kk)
EobCapLbin(kk)
EobCapLBounds(kk,j)
EopUp
;


**LOGICAL CONSTRAINTS
* No Stream Split Conditions


EL(step)..                                      sum(kk$(ord(kk)>  NRAW  AND
ord(kk)<(NRAW+NPROC+1)),y(kk)*PS(kk,step))  =l= 1;
EFeed234..                y('FN2') + y('FNH3') =l= 1;
EFeed2345..               y('FPC') + y('FEC')+ y('FCO2') =l= 1;
EFeedC..                 y('FEO') + y('FPO') + y('FEC') + y('FPC') =l= 1;
*EFeedN2..                 y('FN2') + y('FCO2') =l= 2;
*EFeedEO..                 y('FEO') + y('FCO2') =g= 2;
*EFeedPO..                 y('FPO') + y('FCO2') =g= 2;


* Activation Constraints (big-M notation)
EAc1(i,kk)..          ffdbar(i,kk) =l= y(kk)*M ;
EAc2(i,kk)..          R(i,kk) =l= y(kk)*M ;
```

```
EAc3(kk)..            y(kk)=l=sum((i),ffdbar(i,kk))*M/1000;
EAc4(kk)..            sum(i,Fin(i,kk))=l= y(kk)*M;
*PROCESS INTERVAL MODELS
*Mixing

EIn1(i,k,kk)..        F(i,k,kk) =e= F1(i,k,kk)+F2(i,k,kk) ;
*EIn1(i,k,kk)..         F(i,k,kk) =l= ffdbar(i,k)*S(k,kk)*epsilon(i,k,kk);
EIn2(i,k)$(ord(k)<(NRAW+NPROC+1))..    ffdbar(i,k) =e= sum(kk,F(i,k,kk))
;
EIn3(i,kk)..          Fin(i,kk) =e= sum((k), F(i,k,kk));
EIn4(kk)..            Ftr(kk)   =e= sum(i,ff(i,kk));
EUt1(i,kk)..          R(i,kk) =e= sum(ii,muc(i,ii,kk)* Fin(ii,kk));
EUt2(i,kk)..          ff(i,kk) =l= Fin(i,kk) + alpha(i,kk) * R(i,kk);
*REACTION
ERe(i,kk)..                                                ffbar(i,kk)     =e=
ff(i,kk)+(sum((rr,react),gamma(i,kk,rr)*theta(react,kk,rr)*(ff(react,kk)/MW(re
act))))*MW(i);
*WASTE
EOu(i,kk)$(ord(kk)>NRAW)..  ffdbar(i,kk) =e= ffbar(i,kk)*(1 - SW(i,kk));
EOu2(i,kk)$(ord(kk)>NRAW).. waste(i,kk) =e= ffbar(i,kk)-ffdbar(i,kk);
*Separation
Eout1(i,kk)..         Fout1(i,kk) =e= ffdbar(i,kk)*Split(i,kk);
Eout2(i,kk)..         Fout2(i,kk) =e= ffdbar(i,kk)-Fout1(i,kk);
EFl1(i,k,kk)..        F1(i,k,kk) =l= Fout1(i,k)*SP(k,kk);
EFl2(i,k,kk)..        F2(i,k,kk) =l= Fout2(i,k)*(S(k,kk)-SP(k,kk));
EFl3(i,k)$(ord(k)<(NRAW+NPROC+1))..                        Fout1(i,k)  =e=
sum(kk,F1(i,k,kk));
EFl4(i,k)$(ord(k)<(NRAW+NPROC+1))..                        Fout2(i,k)  =e=
sum(kk,F2(i,k,kk));

*RAW MATERIALS ASSIGNMENT
EFe(i,kk)$(ord(kk)<(NRAW+1))..  ffdbar(i,kk) =e= PHI(i,kk)*y(kk);
```

```
*OBJECTIVE FUNCTION
* Transportation Cost
CostTrans(k,kk)..        Ctr(k,kk) =e= dist(k,kk)*TrPrice*sum(i,F(i,k,kk));
*EobCap(kk)..                                                  Inv(kk)     =e=
(0.0000001+P4('Ac',kk)*sum(i,Fin(i,kk)))**P4('Nc',kk);

EobCapTot..             Capex =e= sum(kk,Invl(kk));
EObSales..             sales =e= sum((i,k),(P3(k)*ffdbar(i,k)));
EObRaw..                rawcost =e= sum((i,kk),(P1(kk)*ffdbar(i,kk)));
EObUtil..              utilcost =e= sum(i,P2(i)*sum(kk,R(i,kk)));
EObTr..                TransCost =e= sum((k,kk),Ctr(k,kk));
EObWaste..              WastePenal =e= WasteCost*sum((i,kk),waste(i,kk));



EobCapInv(kk)..                                              Invl(kk)      =e=
sum((j)$(ord(j)<11),(AlphaLin(j,kk)*Piece(j,kk)+BetaLin(j,kk)*Fpiece(j,kk)))
;   # new
EobCapLflow(kk)..                 Ftr(kk)  =e=  sum((j)$(ord(j)<11),Fpiece(j,kk));
# new
EobCapLbin(kk)..        sum(j,Piece(j,kk))=e=1;
EobCapLBounds(kk,j)$(ord(j)<11)..                  Fpoint(j)*Piece(j,kk)   =l=
Fpiece(j,kk);
EopUp(j,kk)$(ord(j)<11)..               Fpiece(j,kk) =l= Fpoint(j+1)*piece(j,kk);

OBJ..                    Z =e= sales-(rawcost + utilcost)- WastePenal- TransCost-
Capex;



*-------------
* OPTIONS
*-------------
option MINLP= dicopt ;          # Set the MINLP solver
```

```
option optcr=0.;                    # Define the optimality gap
option NLP=conopt;              # Set the NLP subproblem solver
option reslim=1E6;              # Maximum execution time
option domlim=0;                # Number of function evaluation error
option iterlim = 100000;        # Iteration limit

*----------------
*   SOLVE
*----------------

MODEL Model2 /ALL/;
Solve Model2 using MIP maximizing Z;              # Then Solve the MINLP
model
*----------------------------------
*   POST-OPTIMALITY CALCULATIONS
*----------------------------------

Parameters
UtMix(i,kk)
MassDev(i)
MassBalError;

UtMix(i,kk) = alpha(i,kk)*R.l(i,kk);
MassDev(i)     =              sum((kk)$(ord(kk)<(NRAW+1)),ffdbar.l(i,kk))     +
sum((kk),R.l(i,kk)*alpha(i,kk))       -       sum((kk),ffbar.l(i,kk)*SW(i,kk))       -
sum((kk)$(ord(kk)>(NRAW+NPROC)),ffdbar.l(i,kk))   ;
MassBalError = sum(i,MassDev(i));

*------------------
*DISPLAY SOLUTIONS
*------------------
```

```
display y.l, Z.l, sales.l, rawcost.l, utilcost.l, capex.l, TransCost.l, wastePenal.l;
# Results
display F.l,Fin.l,Ftr.l,ff.l,ffbar.l,ffdbar.l,R.l, waste.l;          # Mass
Flows
display                                                               NRAW,
NPROC,Split,SP,gamma,theta,PHI,MW,P1,muc,alpha,P3,P2,P1,S,Sw;         #
Problem definition
display Fpoint, piece.l, Invl.l, alphalin, betalin;
display Fpiece.l;
display  Ctr.l;                               # Other Output
display Utmix, MassDev,MassBalError;                                  #Post
Optimality Calculation
*-------------------
*  EXPORT SOLUTION
*-------------------

execute_unload "OutputFile.gdx";
execute 'gdxxrw.exe OutputFile.gdx var=y.L rng=y! var=F rng=F! var=ff rng=ff!
var=ffbar rng=ffbar! var=ffdbar rng=ffdbar! var=Fin rng=Fin! var=Fout1 rng=Fout1!
var=Fout2 rng=Fout2! var=R rng=R! par=UtMix rng=UtMix! var=sales rng=sales!
var=CTr rng=CTr! var=TransCost rng=TransCost! par=MassBalError
rng=MassBalError! var=rawcost rng=rawcost! var=utilcost rng=utilcost! var=inv
rng=inv! var=Capex rng=Capex!'
```

2. Process simulations of DMC production by urea route

For the DMC production by urea route, the 4 processes are introduced, 1) DMC production by urea route as base case design, 2) intensified process by pervaporation in downstream separation of DMC/MeOH, 3) membrane reactor in DMC synthesis section for removing the NH_3 as by-product and shifting reaction equilibrium and 4) reactive distillation for DMC production by urea and MeOH.

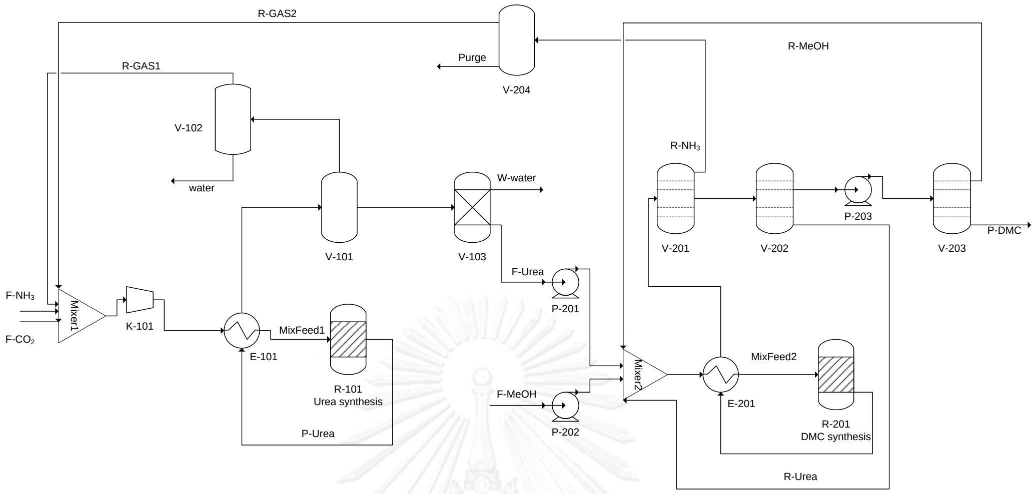

Figure 3. DMC production process by urea route obtained from the superstructure which is the base case design.

The details of my 2nd work is given here; process data for the urea route were obtained through process simulation and formed the basis for design decisions. For the simulation of this base case, the total number of equipment considered was 16 units with 30 streams and 7 compounds. The extended electrolytic UNIQUAC equation is used to describe nonideality of liquid phase, which is NH_3–CO_2–H_2O–Urea mixture under high pressure and high temperature, while the perturbed-hard-sphere (PHS) equation of state is used to predict the fugacity coefficients of the vapor in the VLE calculation of CO_2-NH_3-Urea system (Zhang, Zhang, Yao, & Yuan, 2005). Missing data for pure compound properties and binary interaction parameters of DMC/MeOH, were collected from literatures and calculated through Aspen properties.

Section 1: Urea is synthesized from ammonia and carbon dioxide in the first reactor. This process can utilize 3435 kg/hr of CO_2 coupling reaction with NH_3 3069 kg/hr for producing 4612 kg/hr of urea. The feed stream to reactor (with additional recycled stream) molar ratio of NH_3: CO_2 was 2:1. The simulation revealed a high urea yield of 76.8% when the reactor is operated at 180 bar and 200 ˚C. The value agrees well with the experimental data (70%) reported by Zhang, Zhang, Yao, & Yuan, 2005. The reaction product stream flows into separators V-101 and V-102 for recovery and recycle of the unreacted raw materials. The removal of water to obtain purified urea is done in a separator V-103.

Section 2: In this section, urea and methanol reacted to produce DMC. The feed streams contain 4565 kg/hr of urea and 4361 kmol/hr of MeOH and some of urea and MeOH which remain in the recycle stream. The reactor is operated at 140 ˚C and 8 bar, assuming equilibrium reaction. Yield of DMC achieved is 67.4%, which is similarly close to the experimental data of 67.4% (Sun, Yang, Wang, Wang, & Lin, 2005). The product stream flows to the separation and purification section having azeotropic distillation for DMC/MeOH separation. The first column is a flash separator (V-201) employed to separate NH_3 gas for recycle to the urea synthesis section, the bottom stream contains the unconverted urea 1957 kg/hr, MeOH 2087 kg/hr and DMC 7046 kg/hr. Then, the product stream is sent to the series of pressurized distillation columns (V-202 and V-203) to separate the azeotropic mixture of DMC/MeOH. The production rate of this base case design is 6071 kg/hr (67.4 kmol/hr) with the 99% wt purity. The mass balance of this base case design is given in Table 1.

Table 1. The mass balance of DMC production by urea route (base case in 2nd Work). We can achieve 6071 kg/hr (99.1%wt) with conventional pressurized distillation column.

	F-CO2	F-MEOH	UREA	R-GAS1	F-NH3	P-DMC	P-UREA	R-MEOH	R-UREA	W-WATER
Temperature °C	25	25	184.3	25	25	179.4	200	136.3	213.2	-9.2
Pressure bar	1	1	1	1	1	1	180	10	4	1
Vapor Fraction	1	0	0	1	1	0	0.383	0	0.09	0
Mole Flow kmol/hr	78.062	136.105	76.786	41.726	180.212	69.409	223.2	69.409	29.377	104.078
Mass Flow kg/hr	3435.49	4361.086	4579.373	1302.493	3069.109	6125.427	7807.092	2539.397	1924.019	1913.877
Volume Flow cum/hr	1935.091	5.5	3.977	1034.359	4467.303	7.687	192.696	3.742	28.322	2.059
Enthalpy GJ/hr	-30698	-32451.1	-24593.6	-9535.34	-8267.58	-39467.7	-54458.9	-17556.1	-10564.6	-25363.4
Mass Flow kg/hr										
CO2	3435.49	0	0	965.49	0	0	1021.027	0	0	55.537
H3N	0	0	0.002	337.003	3069.109	0	790.218	1.148	0	453.213
UREA	0	0	4565.644	0	0	0.002	4612.273	0	1439.92	46.118
H2O	0	0	13.727	0	0	13.727	1383.574	0.276	0.24	1359.009
MeOH	0	4361.086	0	0	0	39.73	0	2046.572	0.758	0
DMC	0	0	0	0	0	6071.967	0	491.401	483.101	0
Mass Fraction										
CO2	1	0	0	0.741263	0	0	0.130782	0	0	0.029018
H3N	0	0	4.37E-07	0.258737	1	0	0.101218	0.000452	0	0.236804
UREA	0	0	0.997002	0	0	3.27E-07	0.59078	0	0.748392	0.024097
H2O	0	0	0.002998	0	0	0.002241	0.17722	0.000109	0.000125	0.710082
MeOH	0	1	0	0	0	0.006486	0	0.805928	0.000394	0
DMC	0	0	0	0	0	0.991272	0	0.193511	0.25109	0

3. Additional data for all simulation processes of the urea routes

The 1st process alternative for process intensification is by replacing the conventional pressurized distillation column with the pervaporation unit using crosslinked poly(vinyl alcohol) (PVA) membranes and poly(acrylic acid)/poly(vinyl alcohol) blended membranes (Wang, Li, Lin, & Chen, 2007, 2009) as given in Figure 4.

The azeotrope of DMC/MeOH has been reported in many works. The followings provide the data reported in for systems of pervaporation membrane and reactive distillation.

The 1st one is about the use of crosslinked PVA membranes.

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Crosslinked poly(vinyl alcohol) membranes for separation of dimethyl carbonate/methanol mixtures by pervaporation

Luying Wang, Jiding Li*, Yangzheng Lin, Cuixian Chen

Department of Chemical Engineering, Tsinghua University, Beijing 100084, PR China

From Wang *et al*., (2009), there is an azeotropic mixture of DMC/MeOH in the downstream separation system. Therefore the pervaporation membrane unit was required to reduce the energy consumption due to this azeotrope. The results demonstrated that the crosslinked PVA membrane prepared in this work had an excellent selectivity: the MeOH concentration in permeate side was always higher than 98.6 wt.% for separating feed mixtures of 40–70 wt.% MeOH at 50–70 ◦C.

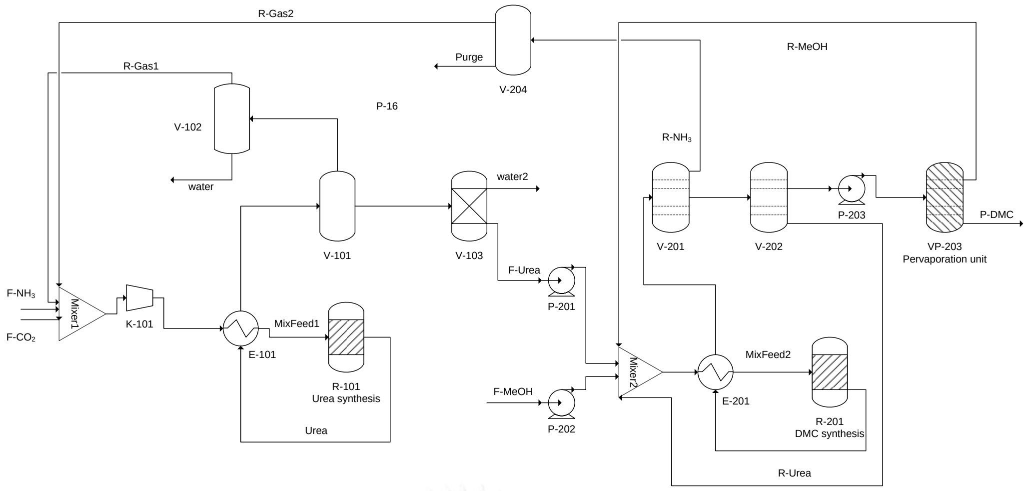


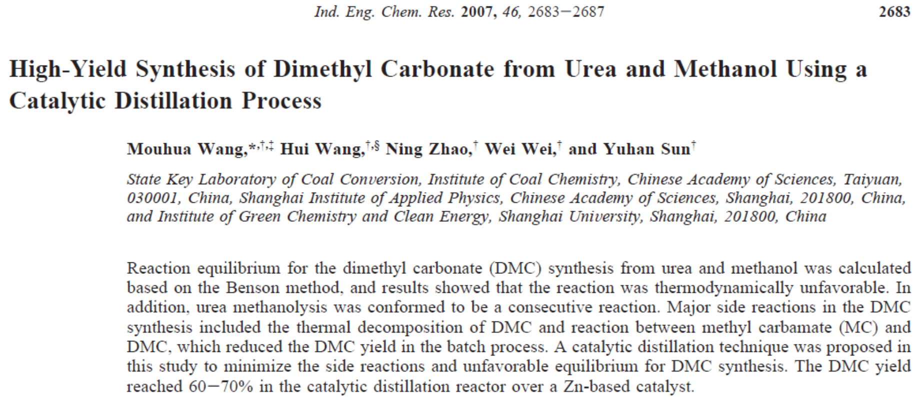
Figure 4. DMC production process by urea route - process alternative 1 using pervaporation unit (VP-204) in downstream separation

The results revealed that the use of crosslinked PVA membrane could achieve high concentration of MeOH of 98.6 wt.%. This process alternative, the feed stream in the permeate side from the feed mixture require the specification of containing 40–70 wt.% MeOH at 50–70 ˚C. Therefore, the pervaporation (VP-204) (as shown in Figure 4S) was set for the separation of DMC/MeOH azeotrope mixture instead of using the conventional pressurized distillation column (V-203) in the base case for reducing energy consumption which can refer to the less amount of methanol flowrate. The azeotropic mixture was flown from the distillate stream of V-202 to the pervaporation unit with a flowrate of 8434 kg/hr. The pressure at the upstream side and the downstream side in the pervaporation unit was maintained at about 2 bar and 0.2 bar, respectively. According to the simulation, the permeate side was methanol flowing at 2057 kg/hr that was recycled back to the separation section. The remaining of methanol was 29.21 kg/hr in the product stream and DMC achieved as the product is 6072 kg/hr with 99.50% wt purity of DMC. The mass balance of this process is given in Table 2.

Table 2. The mass balance of DMC production by urea route (1st intensified process). We can achieve 6072 kg/hr (99.5%wt) with pervaporation unit in downstream separation of azeotropic mixture of DMC/MeOH.

	F-CO2	F-MEOH	F-UREA	FEEDR	F-NH3	P-DMC	P-UREA	R-MEOH	R-UREA	W-WATER
Temperature °C	25	25	184.3	25	25	70	200	70	212.2	-9.2
Pressure bar	1	1	1	1	1	1	18	1	4	1
Vapor Fraction	1	0	0	1	1	0	0.383	1	0.085	0
Mole Flow kmol/hr	78.062	135.777	76.786	41.726	180.212	68.325	223.2	75.699	29.376	104.078
Mass Flow kg/hr	3435.49	4350.579	4579.373	1302.493	3069.109	6101.69	7807.092	2333.146	1911.1	1913.877
Volume Flow cum/hr	1935.091	5.487	3.977	1034.359	4467.303	6.252	192.696	2159.733	26.871	2.059
Enthalpy GJ/hr	-30698	-32371.6	-24593.6	-9535.34	-8267.58	-40643.4	-54458.9	-15819.7	-10518.6	-25363.4
Mass Flow kg/hr										
CO2	3435.49	0	0	965.49	0	0	1021.027	0	0	55.537
H3N	0	0	0.002	337.003	3069.109	0	790.218	1.148	0	453.213
UREA	0	0	4565.644	0	0	0	4612.273	0.003	1439.917	46.118
H2O	0	0	13.727	0	0	0	1383.574	188.73	3.451	1359.009
MeOH	0	4350.579	0	0	0	29.207	0	2057.042	0.799	0
DMC	0	0	0	0	0	6072.482	0	86.222	466.933	0
Mass Fraction										
CO2	1	0	0	0.741263	0	0	0.130782	0	0	0.029018
H3N	0	0	4.37E-07	0.258737	1	0	0.101218	0.000492	0	0.236804
UREA	0	0	0.997002	0	0	0	0.59078	1.29E-06	0.753449	0.024097
H2O	0	0	0.002998	0	0	0	0.17722	0.080891	0.001806	0.710082
MeOH	0	1	0	0	0	0.004787	0	0.88166	0.000418	0
DMC	0	0	0	0	0	0.995213	0	0.036955	0.244327	0

The 2nd alternative for process intensification shown in Figure 5 focused on DMC synthesis reactor.



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High-Yield Synthesis of Dimethyl Carbonate from Urea and Methanol Using a Catalytic Distillation Process

Mouhua Wang,[*,†,‡] **Hui Wang,**[†,§] **Ning Zhao,**[†] **Wei Wei,**[†] **and Yuhan Sun**[†]

State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, China, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, China, and Institute of Green Chemistry and Clean Energy, Shanghai University, Shanghai, 201800, China

Reaction equilibrium for the dimethyl carbonate (DMC) synthesis from urea and methanol was calculated based on the Benson method, and results showed that the reaction was thermodynamically unfavorable. In addition, urea methanolysis was conformed to be a consecutive reaction. Major side reactions in the DMC synthesis included the thermal decomposition of DMC and reaction between methyl carbamate (MC) and DMC, which reduced the DMC yield in the batch process. A catalytic distillation technique was proposed in this study to minimize the side reactions and unfavorable equilibrium for DMC synthesis. The DMC yield reached 60−70% in the catalytic distillation reactor over a Zn-based catalyst.

This catalytic distillation process has many benefits, because urea (or MC) has a high melting (or boiling) point, it moved downward and through the reactive section. As reactions took place between urea, MC, and methanol, DMC and ammonia was produced; they were withdrawn from the reaction zone as soon as they were produced by distillation, because the boiling points of ammonia and DMC-methanol azeotrope are much lower than that of urea or MC. As a result, this process could enhance the DMC yield by 1) shifting the reaction equilibrium and 2) minimizing the side reactions of DMC.

Calculations of thermodynamic equilibrium showed that the reaction of urea with methanol is thermodynamically unfavorable for DMC synthesis. The urea methanolysis reaction was found to be a consecutive reaction. Major side reactions included the thermal decomposition of DMC and reaction between MC and DMC, which reduced the DMC yield. The highest DMC yield was measured about 35% over a ZnO catalyst in the batch process. In comparison, catalytic distillation reactor effectively increased the DMC yield by stripping off DMC from the reaction zone, which also minimized the side reactions simultaneously. The highest DMC yield reached 70% over a Zn based catalyst using catalytic distillation in this study. The catalytic distillation process demonstrated a stable performance and a substantial improvement in the DMC yield compared with the batch process.

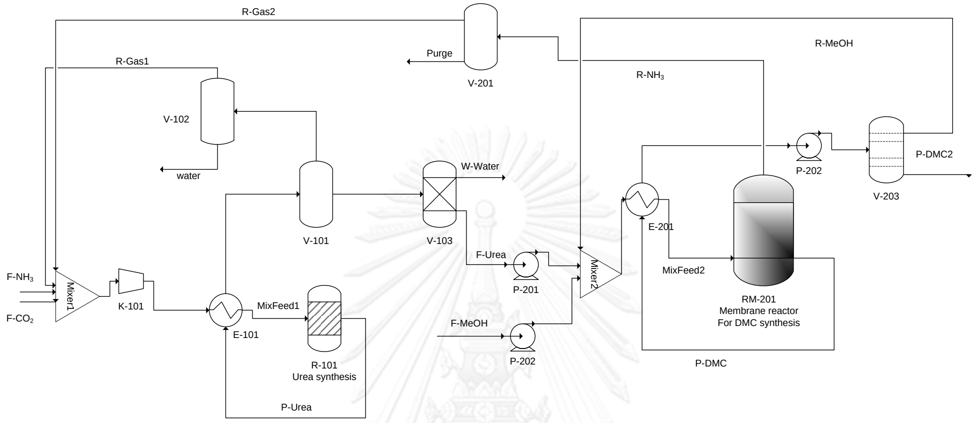

Figure 5. DMC production process by urea route - process alternative 2 using membrane reactor (RM-201) for NH_3 removal.

The use of a membrane catalytic reactor (RM-201) that can draw by-product (i.e., NH3) out of the reactor to shift the reaction equilibrium (Wang, Wang, Zhao, Wei, & Sun, 2007) can significantly increase DMC yield. The reaction occurs at 12 bar 185 ˚C with a MeOH: Urea feed molar ratio of 2.6: 1 and a reflux ratio of 2. The simulation results show that this catalytic reactor offers DMC yield of 80% (with recycled stream). The product stream was sent to the separation and purification section to achieve 5924.8 kg/hr (65.83 kmol/hr) with 99.97%wt purity of DMC. The mass balance of this process is given in Table 3.

Table 3. The mass balance of DMC production by urea route (2nd intensified process). We can achieve 5924.8 kg/hr (99.97%wt) with in-situ removal of NH_3 from membrane reactor.

	F-CO2	F-NH3	P-UREA	F-MEOH	F-UREA	P-DMC	P-DMC2	R-NH3	R-MEOH	W-WATER
Temperature C	25	25	200	25	25	162.4	222.3	85.7	169.3	-9.2
Pressure bar	1	1	18	1	1	12	20	12	20	1
Vapor Frac	1	1	0.383	0	0	0	0	1	0	0
Mole Flow kmol/hr	78.062	180.212	223.2	200	76.024	100	65.84	176.786	34.16	104.078
Mass Flow kg/hr	3435.49	3069.109	7807.092	6408.432	4579.397	7601.373	5924.808	3386.43	1676.569	1913.877
Volume Flow cum/hr	1935.091	4467.303	192.696	8.082058	3.360994	9.422	8.453	439.556	2.395	2.059
Enthalpy GJ/hr	-30698	-8267.58	-54458.9	-47685.5	-25349.9	-55195.1	-40164.1	-10752.3	-16503.5	-25363.4
Mass Flow kg/hr										
CO2	3435.49	0	1021.027	0	0	0	0	0	0	55.537
H3N	0	3069.109	790.218	0	0	0	0	2589.364	0	453.213
UREA	0	0	4612.273	0	4565.67	0	0	0.033	0	46.118
H2O	0	0	1383.574	0	13.727	13.659	1.482	0.068	12.177	1359.009
MeOH	0	0	0	6408.432	0	746.339	0	790.332	746.339	0
DMC	0	0	0	0	0	6841.087	5923.044	6.633	918.048	0
Mass Fraction									0	
CO2	1	0	0.130782	0	0	0	0	0	0	0.029018
H3N	0	1	0.101218	0	0	0	0	0.764629	0	0.236804
UREA	0	0	0.59078	0	0.997002	0	0	9.74E-06	0	0.024097
H2O	0	0	0.17722	0	0.002998	0.001797	0.00025	2.01E-05	0.007263	0.710082
MeOH	0	0	0	1	0	0.098185	0	0.233382	0.445159	0
DMC	0	0	0	0	0	0.89998	0.999702	0.001959	0.547575	0

The 3rd alternative process shown in Figure 6 focused on integration of reaction and separation to reduce the number of unit operations and to increase the yield of DMC and energy efficiency.

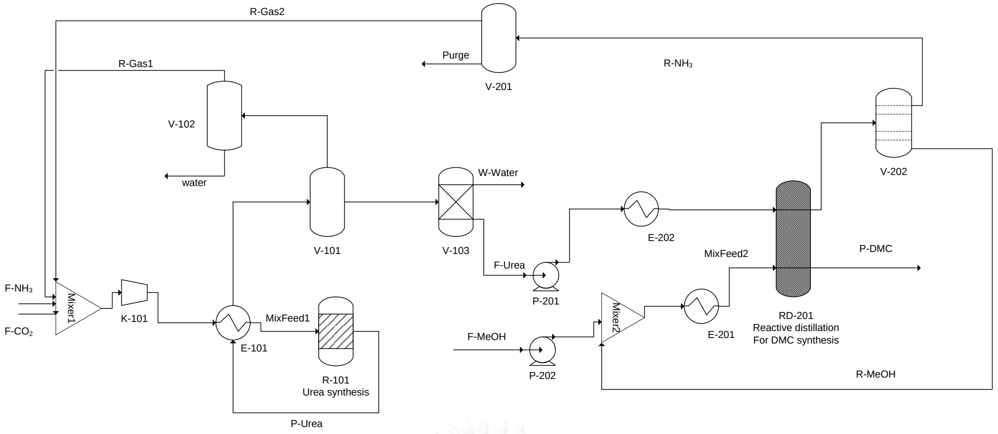

Figure 6. DMC production process by urea route which is the process alternative 3 using reactive distillation (RD-201) for integrating reaction and separation system.

Reactive distillation is used in this alternative (Wang, Zhao, Xiao, Wei, & Sun, 2012). The feed streams contain 4565 kg/hr of urea and 5126 kg/hr of MeOH plus with the recycled MeOH from downstream separation at the molar ratio of urea: MeOH of 2:1. The reactive distillation (RD-201) had 40 stages, whereas the reaction zone was at stages 17-22. Urea was fed at stage 16 and MeOH was fed at stage 26. The distillate stream, which contains NH_3, urea, MeOH and DMC was sent to the flash separator to separate and recycle NH_3 to the urea synthesis section, the unreacted urea, MeOH and some DMC product would be recycled and sent to the reaction section. For the DMC product which is the bottom stream of DMC synthesis reactor has the production rate of 6190 kg/hr (69.10 kmol/hr). This process resulted in very high yield of DMC (97.5%) and high purity of DMC in the product 99.88% wt. The mass balance of this process is given in Table 4.

Table 4. The mass balance of DMC production by urea route (3rd intensified process). We can achieve 6190 kg/hr (99.88%wt) v reactive distillation unit.

	F-CO2	F-NH3	P-UREA	F-MEOH	F-UREA	P-DMC	R-NH3	R-MEOH	W-WATER
Temperature C	25	25	200	25	25	192.8	-31.5	88.6	-9.2
Pressure bar	1	1	18	1	1	12	1	1	1
Vapor Fraction	1	1	0.383	0	0	0	0	0	0
Mole Flow kmol/hr	78.062	180.212	223.2	144.44	76.786	69.107	167.074	61.819	104.078
Mass Flow kg/hr	3435.49	3069.109	7807.092	4628.184	4579.397	6197.024	3489.696	4857.48	1913.877
Volume Flow cum/hr	1935.091	4467.303	192.696	5.837	3.376	8.042	4.667	5.091	2.059
Enthalpy GJ/hr	-30698.008	-8267.58	-54458.9	-34413.4	-25568.4	-39635	-17187.9	-33689.6	-25363.4
Mass Flow kg/hr									
CO2	3435.49	0	1021.027	0	0	0	0	0	55.537
H3N	0	3069.109	790.218	0	0	0	2589.463	0.627	453.213
UREA	0	0	4612.273	0	4565.67	0	0	0	46.118
H2O	0	0	1383.574	0	13.727	7.022	6.705	168.353	1359.009
MeOH	0	0	0	4628.184	0	0	235.473	19.323	0
DMC	0	0	0	0	0	6190.003	658.056	4669.178	0
Mass Fraction									
CO2	1	0	0.130782	0	0	0	0	0	0.029018
H3N	0	1	0.101218	0	0	0	0.742031	0.000129	0.236804
UREA	0	0	0.59078	0	0.997002	0	0	0	0.024097
H2O	0	0	0.17722	0	0.002998	0.001133	0.001921	0.034659	0.710082
MeOH	0	0	0	1	0	0	0.067477	0.003978	0
DMC	0	0	0	0	0	0.998867	0.188571	0.961235	0

4. Process simulations of DMC production by EC route (these processes were given in supplementary data)

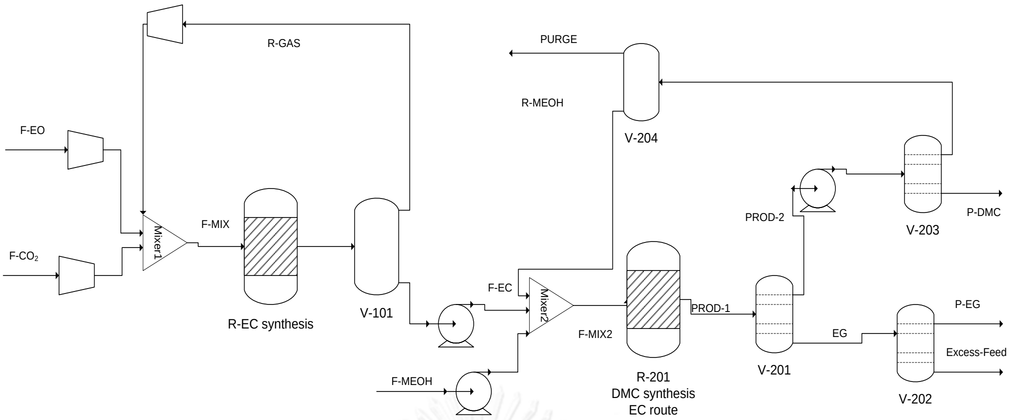

Figure 8. Process flow diagram for the ethylene carbonate route for dimethyl carbonate production as base case design. The mass balance for this process is given in Table 5 (same process as represent in previous work but has higher production rate).

Table 5. The mass balance of DMC production by EC route (base case Work2). We can achieve 5737 kg/hr (99.3%wt) of DMC but obtain 3708 kg/hr (93.2%wt) of EG due to the presence of azeotrope of EC/EG.

	F-CO2	F-EO	F-EC	F-MEOH	F-MIX2	PRD-EGEC	PROD-DMC	PROD-EG	EXCS-FEC	R-MEOH	R-GAS
Temperature C	25	25	248	25	126.4	191.7	161.5	292.8	312.2	123.4	132.7
Pressure bar	1	1	1	1	7	1	7	10	10	7	1
Vapor Fraction	1	1	0	0	0	0	0	0	0	0	1
Mole Flow kmol/hr	77.04	77.04	77	133.984	229.884	78.434	65	62.8	12.634	21	139.72
Mass Flow kg/hr	3390.515	3393.86	6780.85	4293.128	11846.935	5208.653	5779.43	3978.147	1014.335	858.852	6317.013
Volume Flow cum/hr	1909.758	1909.76	6.155	5.414	12.636	5.301	6.96	4.747	1.06	1.174	4714.212
Enthalpy MJ/hr	-30296.3	-4050.11	-40999	-31919.736	-78240.8	-35237.648	-37379.86	-26020.296	-6121.19	-5916.18	-50316.8
Mass Flow kg/hr											
CO2	3390.515	0	0	0	0	0	0	0	0	0	5411.445
EO	0	3393.86	0	0	0	0	0	0	0	0	570.929
EC	0	0	6780.85	0	6780.848	1017.127	0	225.696	779.757	0	334.639
MEOH	0	0	0	4293.128	4806.324	0.002	41.791	0	0	570.213	0
DMC	0	0	0	0	259.763	129.144	5737.64	43.826	0.03	288.639	0
EG	0	0	0	0	0	4062.379	0	3708.625	234.548	0	0
Mass Fraction											
CO2	1	0	0	0	0	0	0	0	0	0	0.856646
EO	0	1	0	0	0	0	0	0	0	0	0.09038
EC	0	0	1	0	0.5723715	0.1952764	0	0.05673395	0.768737	0	0.052974
MEOH	0	0	0	1	0.4057019	3.8398E-07	0.007231	0	0	0.663925	0
DMC	0	0	0	0	0.0219266	0.02479413	0.9927692	0.01101669	2.96E-05	0.336075	0
EG	0	0	0	0	0	0.7799289	0	0.93224936	0.231233	0	0

For DMC production by ethylene carbonate route with intensification. The process alternative has been establish the reactor unit for intensifying the product yield, max conversion of reactant, less raw material remaining in product stream and no solvent usage due to waste minimization concept.

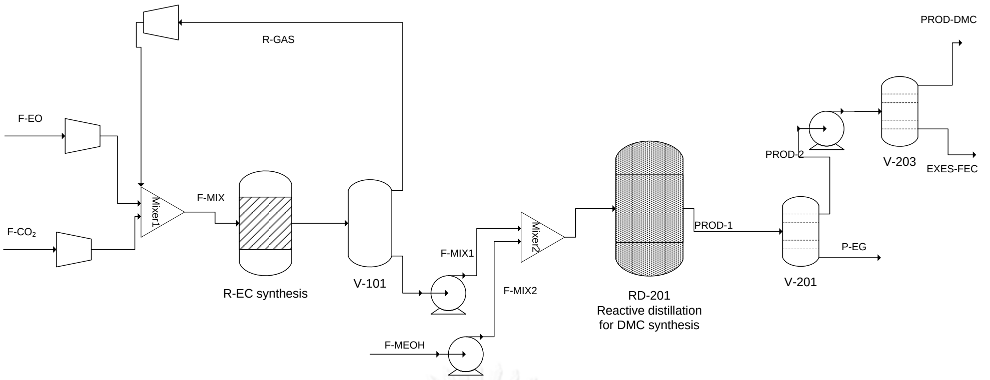

Figure 9. Process flow diagram for the ethylene carbonate route for dimethyl carbonate production using reactive distillation (RD-201). The mass balance for this process is given in Table 6.

For DMC production by ethylene carbonate route via reactive distillation


Computers and Chemical Engineering 34 (2010) 361–373

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Plant-wide design and control of DMC synthesis process via reactive distillation and thermally coupled extractive distillation

San-Jang Wang[a,*], Cheng-Ching Yu[b], Hsiao-Ping Huang[b]

[a] Department of Chemical and Material Engineering, Ta Hwa Institute of Technology, No. 1, Ta Hwa Road, Chiunglin, Hsinchu 307, Taiwan
[b] Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

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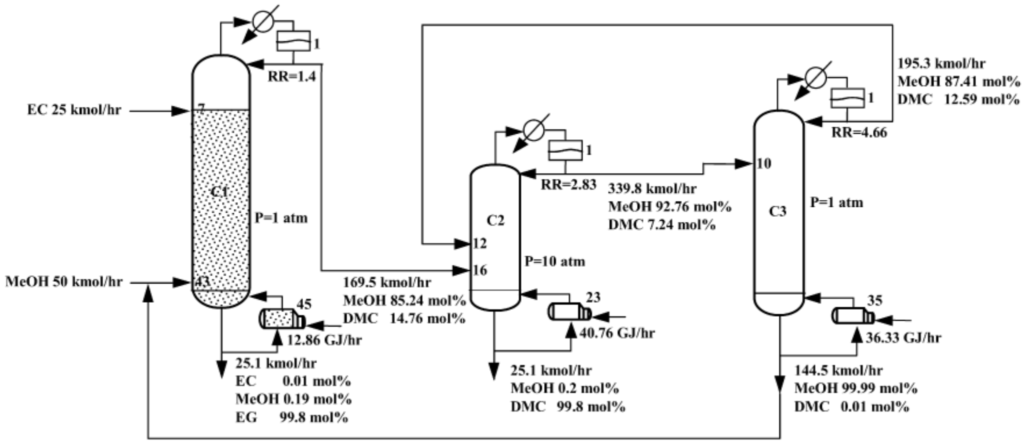


Fig. 1. Process flowsheet of reactive distillation + pressure-swing distillation.

The verification result of this process and the reference journal are comparable. The feed stream contain 6780 kg/hr of EC and 4806 kg/hr of MeOH were send to reactive distillation (RD-201) which have nearly 100% conversion of EC. his phenomenon has benefit because it can avoid azeotrope of DMC/MeOH and EC/EG which has high energy consumption in downstream separation of this process.

The EG product (bottom product) will separate as the bottom stream of V-201 at 95.6%wt purity not 100%wt due to the azeotrope of some EC. And the distillate stream DMC, have send to pressurized distillation column (V-203) operate at the same operating condition (10 bar) to achieve 100%wt purity of DMC.

Table 6. The mass balance of DMC production by EC route reactive distillation obtain very high yield of DMC 6477 kg/hr (99.99%wt) of DMC but obtain 4329 kg/hr (95.6%wt) of EG due to the presence of azeotrope of EC/EG.

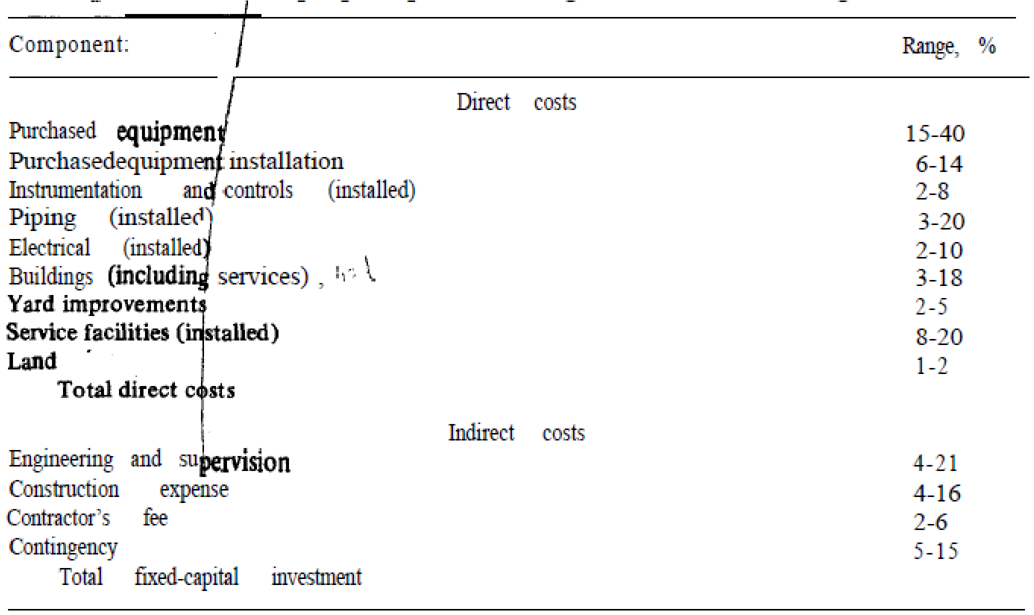
	F-CO2	F-EC	F-EO	F-MEOH	F-MIX	F-MIX1	F-MIX2	PROD-DMC	PROD-EG	R-GAS	EXCES-FD
Temperature C	25	248	25	25	577.4	248.1	25.1	89.8	293.4	132.7	126.4
Pressure bar	1	1	1	1	125	10	10	1	10	1	1
Vapor Fraction	1	0	1	0	1	0	0	0	0	1	0
Mole Flow kmol/hr	77.04	77	77.04	150	293.76	77	150	71.913	72	139.72	8.087
Mass Flow kg/hr	3390.515	6780.848	3393.855	4806.324	13097.86	6780.848	4806.32	6477.84	4528.185	6317.01	581.147
Volume Flow cum/hr	1909.758	6.155	1909.758	6.062	166.186	6.155	6.063	6.831	5.424	4714.21	0.591
Enthalpy MJ/hr	-30296.3	-40999	-4050.11	-35735.5	-75885.2	-40994.8	-35735.5	-42890.184	-29681.3	-50316.8	-3991.54
Mass Flow kg/hr											
CO2	3390.515	0	0	0	8801.96	0	0	0	0	5411.45	0
EO	0	0	3393.855	0	3964.784	0	0	0	0	570.929	0
EC	0	6780.848	0	0	331.117	6780.848	0	0	169.545	334.639	6.581
MEOH	0	0	0	4806.324	0	0	4806.32	0	0	0	0
DMC	0	0	0	0	0	0	0	6477.84	29.621	0	248.452
EG	0	0	0	0	0	0	0	0	4329.019	0	326.114
Mass Fraction											
CO2	1	0	0	0	0.672015	0	0	0	0	0.85665	0
EO	0	0	1	0	0.302705	0	0	0	0	0.09038	0
EC	0	1	0	0	0.02528	1	0	0	0.037442	0.05297	0.011324
MEOH	0	0	0	1	0	0	1	0	0	0	0
DMC	0	0	0	0	0	0	0	1	0.006541	0	0.42752
EG	0	0	0	0	0	0	0	0	0.956016	0	0.561156

5. Economic evaluation of each process

Data input to ECON in manuscript 2:
Chemical Engineering Plant Cost Index (2013); 567.3
Update factor; 1.453125
Operating day per year; 300 days
Electricity; 16.8 \$/GJ
HP Steam; 9.83 \$/GJ
MP Steam; 8.22 \$/GJ
LP Steam; 7.78 \$/GJ
Cooling Water; 0.35 \$/GJ

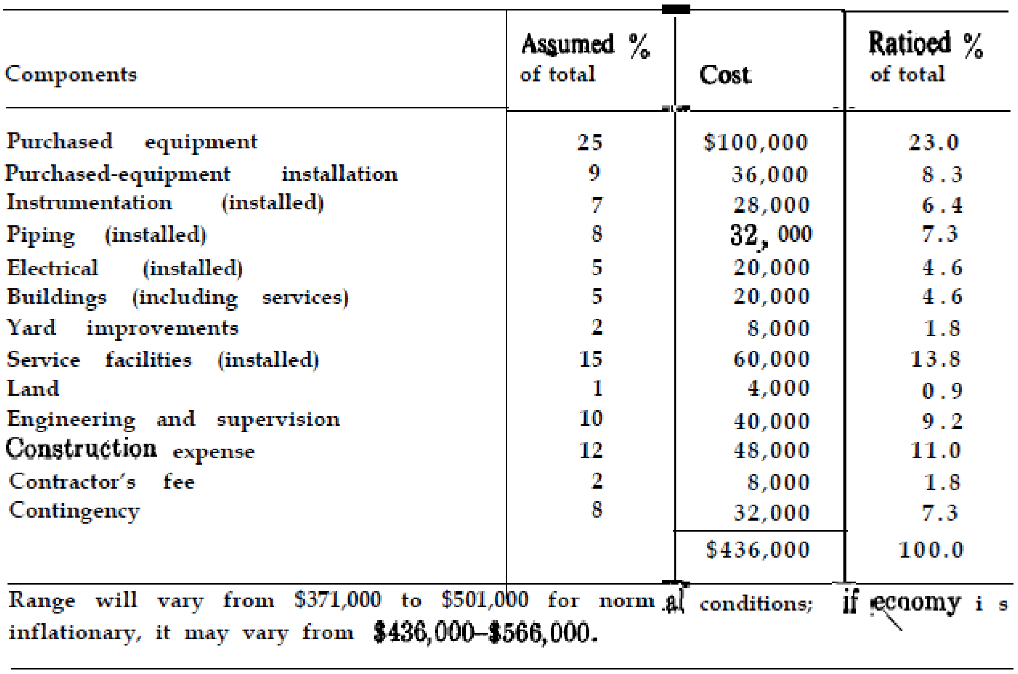
Therefore, the verification of economic analysis in detail were considered and compare toPlant design and economics for chemical engineer (Peters Timmerhaus, 1991).

Table 7. The typical percentage of fixed-capital investment values for direct and indirect cost segment for multipurpose plants or large additions to existing facilities (Timmerhaus, 1991).



Component:	Range, %
Direct costs	
Purchased equipment	15-40
Purchasedequipment installation	6-14
Instrumentation and controls (installed)	2-8
Piping (installed)	3-20
Electrical (installed)	2-10
Buildings (including services)	3-18
Yard improvements	2-5
Service facilities (installed)	8-20
Land	1-2
Total direct costs	
Indirect costs	
Engineering and supervision	4-21
Construction expense	4-16
Contractor's fee	2-6
Contingency	5-15
Total fixed-capital investment	

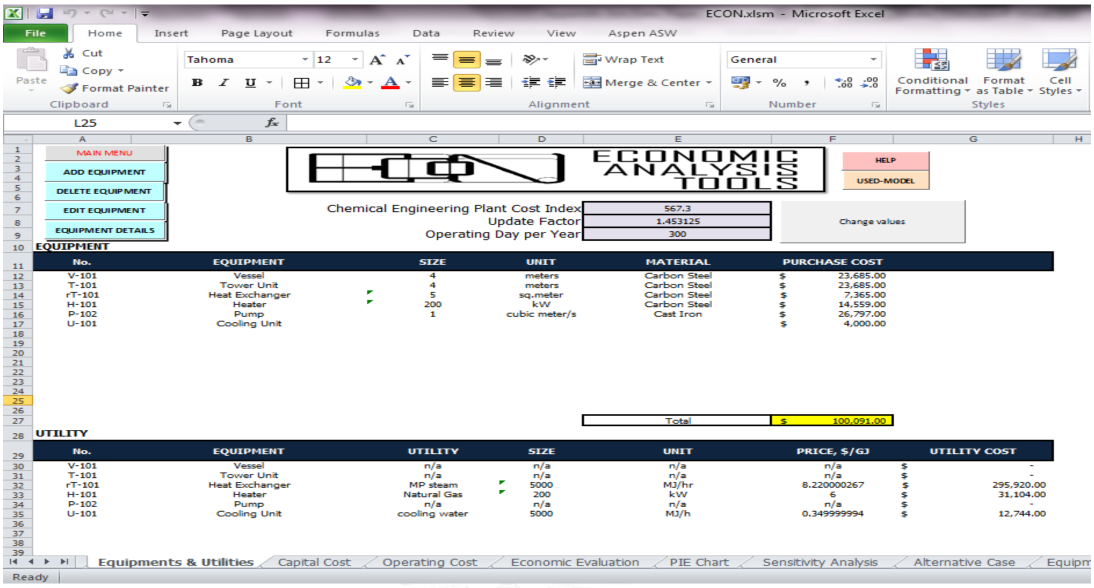
The example of validation on ECON compare to Timmerhaus's book. The total capital cost is reported to 436,000 USD.



Components	Assumed % of total	Cost	Ratioed % of total
Purchased equipment	25	$100,000	23.0
Purchased-equipment installation	9	36,000	8.3
Instrumentation (installed)	7	28,000	6.4
Piping (installed)	8	32,000	7.3
Electrical (installed)	5	20,000	4.6
Buildings (including services)	5	20,000	4.6
Yard improvements	2	8,000	1.8
Service facilities (installed)	15	60,000	13.8
Land	1	4,000	0.9
Engineering and supervision	10	40,000	9.2
Construction expense	12	48,000	11.0
Contractor's fee	2	8,000	1.8
Contingency	8	32,000	7.3
		$436,000	100.0

Range will vary from $371,000 to $501,000 for normal conditions; if economy is inflationary, it may vary from $436,000–$566,000.

The economic analysis to comparison was set up in ECON with these below detail as follow.



Chemical Engineering Plant Cost Index 567.3

Update Factor 1.453125

Operating Day per Year 300

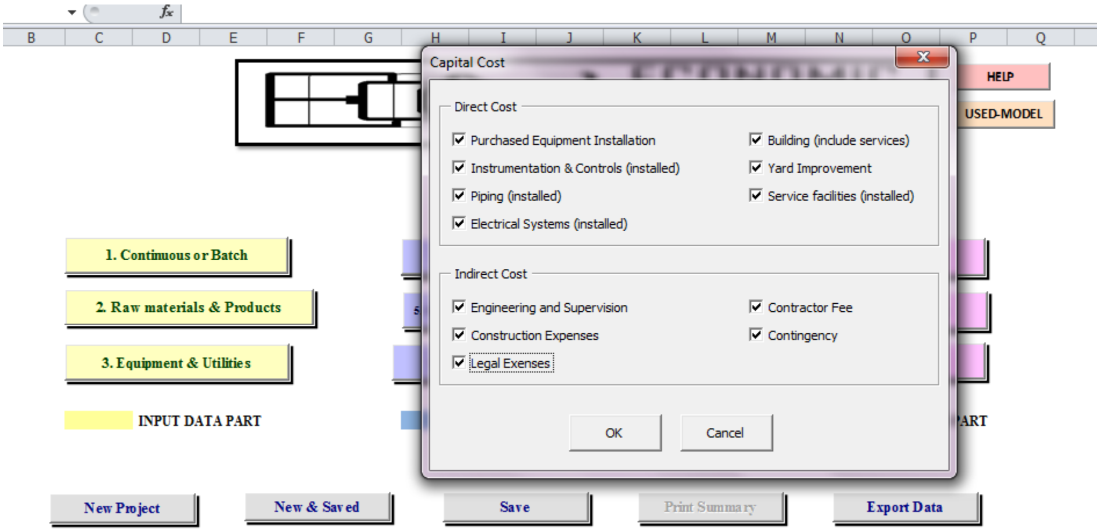
EQUIPMENT

No.	EQUIPMENT	SIZE	UNIT	MATERIAL	PURCHASE COST
V-101	Vessel	4	meters	Carbon Steel	$ 23,685.00
T-101	Tower Unit	4	meters	Carbon Steel	$ 23,685.00
rT-101	Heat Exchanger	5	sq.meter	Carbon Steel	$ 7,365.00
H-101	Heater	200	kW	Carbon Steel	$ 14,559.00
P-102	Pump	1	cubic meter/s	Cast Iron	$ 26,797.00
U-101	Cooling Unit				$ 4,000.00
				Total	$ 100,091.00

UTILITY

No.	EQUIPMENT	UTILITY	SIZE	UNIT	PRICE, $/GJ	UTILITY COST
V-101	Vessel	n/a	n/a	n/a	n/a	$ -
T-101	Tower Unit	n/a	n/a	n/a	n/a	$ -
rT-101	Heat Exchanger	MP steam	5000	MJ/hr	8.220000267	$ 295,920.00
H-101	Heater	Natural Gas	200	kW	6	$ 31,104.00
P-102	Pump	n/a	n/a	n/a	n/a	$ -
U-101	Cooling Unit	cooling water	5000	MJ/h	0.349999994	$ 12,744.00

<u>Figure 10. The example of unit operations and cost evaluation from ECON.</u>



Capital Cost

Direct Cost

☑ Purchased Equipment Installation
☑ Instrumentation & Controls (installed)
☑ Piping (installed)
☑ Electrical Systems (installed)
☑ Building (include services)
☑ Yard Improvement
☑ Service facilities (installed)

Indirect Cost

☑ Engineering and Supervision
☑ Construction Expenses
☑ Legal Exenses
☑ Contractor Fee
☑ Contingency

Figure 11. The user interface of ECON tool; the capital cost evaluation with direct cost and in-direct cost estimation.

Table 8. The total capital cost investment calculation from ECON.

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant		Result
Purchased Equipment Delivered	1.1	$	110,100.10
Purchased Equipment Installation	0.47	$	51,747.05
Instrumentation and Controls (installed)	0.36	$	39,636.04
Piping (Installed)	0.68	$	74,868.07
Electrical Systems (Installed)	0.11	$	12,111.01
Buildings (Including Services)	0.18	$	19,818.02
Yard Improvement	0.1	$	11,010.01
Service Facilities (Installed)	0.7	$	77,070.07
	2.6		
	Total Direct Cost	$	396,360.36
Nonmanufacturing Fixed-capital Investment (Indirect Cost	Percent of Delivered-equipment for Fluid Processing Plant		Result
Engineering and Supervision	0.33	$	36,333.03
Construction Expenses	0.41	$	45,141.04
Legal Expenses	0.04	$	4,404.00
Contractor's Fees	0.22	$	24,222.02
Contingency	0.44	$	48,444.04
	1.44		
	Total indirect cost	$	158,544.14
Fixed-capital Investment	Percent of Delivered-equipment for Fluid Processing Plant		Result
Fixed-capital Investment (FCI)		$	554,904.50
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant		Result
Working Capital Investmenst (WC)	0.89	$	2,202.00
	Total Capital Investment (TCI)	$	557,106.51

From above comparison, the cost evaluation from Plant design and economic book are lower (436,000 USD) and from the ECON software are higher (557,106 USD) this is due to the inflationary or some factors which take into the account for economic analysis. So, the highest possibility of plant design book can be 566,000 USD which are comparable to ECON tool.

Therefore, the economic analysis in this work was calculating by ECON.

DMC production by urea route (Base case).

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result
Purchased Equipment Delivered	1.1	$ 1,415,680.20
Purchased Equipment Installation	0.47	$ 665,369.69
Instrumentation and Controls (installed)	0.36	$ 509,644.87
Piping (Installed)	0.68	$ 962,662.54
Electrical Systems (Installed)	0.11	$ 155,724.82
Buildings (Including Services)	0.18	$ 254,822.44
Yard Improvement	0.1	$ 141,568.02
Service Facilities (Installed)	0.7	$ 990,976.14
	2.6	
	Total Direct Cost	$ 4.04

Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result
Engineering and Supervision	0.33	$ 467,174.47
Construction Expenses	0.41	$ 580,428.88
Legal Expenses	0.04	$ 56,627.21
Contractor's Fees	0.22	$ 311,449.64
Contingency	0.44	$ 622,899.29
	1.44	
	Total indirect cost	$ -

Fixed-capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result

Fixed-capital Investment (FCI)		$	7,135,028.21
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result	
Working Capital Investment (WC)	0.89	$	28,313.60
	Total Capital Investment (TCI)	$	7,163,341.81

Pervaporation of DMC/MeOH in downstream separation of Urea route.

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for	Result	
	Fluid Processing Plant		
Purchased Equipment Delivered	1.1	$	1,171,896.00
Purchased Equipment Installation	0.47	$	550,791.12
Instrumentation and Controls (installed)	0.36	$	421,882.56
Piping (Installed)	0.68	$	796,889.28
Electrical Systems (Installed)	0.11	$	128,908.56
Buildings (Including Services)	0.18	$	210,941.28
Yard Improvement	0.1	$	117,189.60
Service Facilities (Installed)	0.7	$	820,327.20
	2.6		
	Total Direct Cost	$	4.04

Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for	Result	
	Fluid Processing Plant		
Engineering and Supervision	0.33	$	386,725.68
Construction Expenses	0.41	$	480,477.36
Legal Expenses	0.04	$	46,875.84
Contractor's Fees	0.22	$	257,817.12
Contingency	0.44	$	515,634.24
	1.44		
	Total indirect cost	$	-

Fixed-capital Investment	Percent of Delivered-equipment	Result

						for Fluid Processing Plant		
	Fixed-capital Investment (FCI)						$	5,906,355.84
	Working Capital Investment					Percent of Delivered-equipment for Fluid Processing Plant	Result	
	Working Capital Investment (WC)					0.89	$	23,437.92
						Total Capital Investment (TCI)	$	5,929,793.76

Membrane reactor (NH_3 in-situ removal from reactor).

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result	
Purchased Equipment Delivered	1.1	$	985,066.50
Purchased Equipment Installation	0.47	$	462,981.26
Instrumentation and Controls (installed)	0.36	$	354,623.94
Piping (Installed)	0.68	$	669,845.22
Electrical Systems (Installed)	0.11	$	108,357.32
Buildings (Including Services)	0.18	$	177,311.97
Yard Improvement	0.1	$	98,506.65
Service Facilities (Installed)	0.7	$	689,546.55
	2.6		
	Total Direct Cost	$	4.04
Nonmanufacturing Fixed-capital Investment (Indirect Cost)	**Percent of Delivered-equipment for Fluid Processing Plant**	**Result**	
Engineering and Supervision	0.33	$	325,071.95
Construction Expenses	0.41	$	403,877.27
Legal Expenses	0.04	$	39,402.66
Contractor's Fees	0.22	$	216,714.63
Contingency	0.44	$	433,429.26
	1.44		
	Total indirect cost	$	-
Fixed-capital Investment	**Percent of Delivered-equipment**	**Result**	

	for Fluid Processing Plant		
Fixed-capital Investment (FCI)		$	4,964,735.16
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result	
Working Capital Investment (WC)	0.89	$	19,701.33
	Total Capital Investment (TCI)	$	4,984,436.49

Reactive distillation for urea route (intensified urea route).

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant		Result
Purchased Equipment Delivered	1.1	$	773,119.60
Purchased Equipment Installation	0.47	$	363,366.21
Instrumentation and Controls (installed)	0.36	$	278,323.06
Piping (Installed)	0.68	$	525,721.33
Electrical Systems (Installed)	0.11	$	85,043.16
Buildings (Including Services)	0.18	$	139,161.53
Yard Improvement	0.1	$	77,311.96
Service Facilities (Installed)	0.7	$	541,183.72
	2.6		
	Total Direct Cost	$	4.04
Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for Fluid Processing Plant		Result
Engineering and Supervision	0.33	$	255,129.47
Construction Expenses	0.41	$	316,979.04
Legal Expenses	0.04	$	30,924.78
Contractor's Fees	0.22	$	170,086.31
Contingency	0.44	$	340,172.62
	1.44		
	Total indirect cost	$	-
Fixed-capital Investment	Percent of Delivered-equipment		Result

	for Fluid Processing Plant	
Fixed-capital Investment (FCI)		$ 3,896,522.78
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result
Working Capital Investment (WC)	0.89	$ 15,462.39
	Total Capital Investment (TCI)	$ 3,911,985.18

DMC production by EC route (base case for EC route).

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result	
Purchased Equipment Delivered	1.1	$	1,074,592.20
Purchased Equipment Installation	0.47	$	505,058.33
Instrumentation and Controls (installed)	0.36	$	386,853.19
Piping (Installed)	0.68	$	730,722.70
Electrical Systems (Installed)	0.11	$	118,205.14
Buildings (Including Services)	0.18	$	193,426.60
Yard Improvement	0.1	$	107,459.22
Service Facilities (Installed)	0.7	$	752,214.54
	2.6		
	Total Direct Cost	$	3,868,531.92
Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result	
Engineering and Supervision	0.33	$	354,615.43
Construction Expenses	0.41	$	440,582.80
Legal Expenses	0.04	$	42,983.69
Contractor's Fees	0.22	$	236,410.28
Contingency	0.44	$	472,820.57
	1.44		
	Total indirect cost	$	1,547,412.77
Fixed-capital Investment	Percent of Delivered-equipment	Result	

	for Fluid Processing Plant	
Fixed-capital Investment (FCI)		$ 5,415,944.69
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result
Working Capital Investment (WC)	0.89	$ 21,491.84
	Total Capital Investment (TCI)	$ 5,437,436.53

Reactive distillation for EC route (intensified EC process).

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result
Purchased Equipment Delivered	1.1	$ 781,732.60
Purchased Equipment Installation	0.47	$ 367,414.32
Instrumentation and Controls (installed)	0.36	$ 281,423.74
Piping (Installed)	0.68	$ 531,578.17
Electrical Systems (Installed)	0.11	$ 85,990.59
Buildings (Including Services)	0.18	$ 140,711.87
Yard Improvement	0.1	$ 78,173.26
Service Facilities (Installed)	0.7	$ 547,212.82
	2.6	
	Total Direct Cost	$ 4.04

Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for Fluid Processing Plant	Result
Engineering and Supervision	0.33	$ 257,971.76
Construction Expenses	0.41	$ 320,510.37
Legal Expenses	0.04	$ 31,269.30
Contractor's Fees	0.22	$ 171,981.17
Contingency	0.44	$ 343,962.34
	1.44	
	Total indirect cost	$ -

Fixed-capital Investment	Percent of Delivered-equipment	Result

						for		
						Fluid Processing Plant		
	Fixed-capital Investment (FCI)						$	3,939,932.30
	Working Capital Investment					Percent of Delivered-equipment for	Result	
						Fluid Processing Plant		
	Working Capital Investment (WC)					0.89	$	15,634.65
						Total Capital Investment (TCI)	$	3,955,566.96

BAYER process

Manufacturing Fixed-capital Investment (Direct Cost)	Percent of Delivered-equipment for	Result
	Fluid Processing Plant	
Purchased Equipment Delivered	1.1	$ 535,207.11
Purchased Equipment Installation	0.47	$ 251,547.34
Instrumentation and Controls (installed)	0.36	$ 192,674.56
Piping (Installed)	0.68	$ 363,940.84
Electrical Systems (Installed)	0.11	$ 58,872.78
Buildings (Including Services)	0.18	$ 96,337.28
Yard Improvement	0.1	$ 53,520.71
Service Facilities (Installed)	0.7	$ 374,644.98
	2.6	
	Total Direct Cost	$ 4.04

Nonmanufacturing Fixed-capital Investment (Indirect Cost)	Percent of Delivered-equipment for	Result
	Fluid Processing Plant	
Engineering and Supervision	0.33	$ 176,618.35
Construction Expenses	0.41	$ 219,434.92
Legal Expenses	0.04	$ 21,408.28
Contractor's Fees	0.22	$ 117,745.57
Contingency	0.44	$ 235,491.13
	1.44	
	Total indirect cost	$ -

Fixed-capital Investment	Percent of Delivered-equipment for	Result

	Fluid Processing Plant	
Fixed-capital Investment (FCI)		$ 2,697,443.86
Working Capital Investment	Percent of Delivered-equipment for Fluid Processing Plant	Result
Working Capital Investment (WC)	0.89	$ 10,704.14
	Total Capital Investment (TCI)	$ 2,708,148.00

Economic evaluation of each process alternative.

	Base case: urea route	**Prc 1 (Pervap)**	**Prc 2 (MBR)**	**Prc 3 (RD)**	**Base case: EC route**	**Intensified EC route**	**BAYER process**
Economic indicators *(analysis in CO_2 utilization section and DMC production section)*							
Production cost/kg of product (USD/kg)							
DMC	0.7563	0.7216	0.6823	0.6499	0.9307	0.7834	0.5908
EG	-	-	-	-	0.9352	0.8017	-
Total sale prices; *calculated from products prices x production rate (USD/yr)*	52461734.4	52466227.2	51184742.4	53194320.0	84283538.4	97845451.2	33466089.6
Total cost; *calculated from Fixed capital cost + operating cost (utilities) + Raw material cost (USD/yr)*	33064514.0	31552815.0	30244488.0	28809448.0	63295829.0	61742620.0	16481700.0
Net profit margin; *calculated from Total sale price – Total cost (USD/yr)*	19397220.4	20913412.2	20940254.4	24384872.0	20987709.4	36102831.2	16984389.6
Profit (USD/kg)							
DMC	0.4437	0.4784	0.5177	0.5501	0.2693	0.4166	0.6092
EG	-	-	-	-	0.3648	0.4983	-
Fixed-capital Investment (USD/yr)	7163341	5929793	4984436	3911958	5437436	3955566	2708148
Operating cost (USD/yr)	632053	606592	496314	386444	517023	445684	298061
Raw material cost (USD/yr)	25269120	25016430	24763738	24511046	57341370	57341370	13475491
Cooling water usage (GJ/yr)	194954.4	116424.0	118958.4	81172.8	132602.4	121910.4	98496
Fuel usage (GJ/yr)	295783.2	243187.2	177696.0	153813.6	285235.2	284104.8	175824
CO_2 usage in process as raw material (MT/yr)	24732.0	24732.0	24732.0	24732.0	24411.6	24411.6	-

Performance evaluation of each process alternative (Urea route is the base case).

	energy consumption/kg of DMC	Fixed-capital investment	Operating cost	CO2 emission	HTC	GWP	Raw material cost	(Cold utilities) water usage	(Hot utilities) Steam usage
Urea Base case	1	1	1	1	1	1	1	1	1
Pervaporation	0.7949387	0.831985	0.959718172	0.521220159	0.875817	0.802297	0.99	0.597185803	0.82218057
membrane reactor	0.5722013	0.695826	0.785241111	0.40606959	0.820261	0.749437	0.98	0.610185767	0.600764344
reactive distillation	0.5128948	0.546108	0.611411543	0.195974411	0.800654	0.594967	0.97	0.416368135	0.520021421
EC base case	0.7437458	0.759064	0.818005769	0.322437198	1.48366	1.183517	2.269227025	0.680171363	0.964338745
EC intensified option	0.5689172	0.552196	0.705137069	0.293337494	1.183007	0.688133	2.269227025	0.625327769	0.960517027
BAYER	1.0190283	0.378057	0.47157596	0.194414105	1.611111	0.508894	0.770722961	0.505225837	0.594435384

Life cycle assessment of each process alternative.

Sustainability metrics	**Base case: urea route**	**Prc 1 (Pervap)**	**Prc 2 (MBR)**	**Prc 3 (RD)**	**Base case: EC route**	**Intensified EC route**	**BAYER process**
Life cycle assessment indicator							
CO_2 emission from process (MT/yr)	80769.87	53942.57	46933.38	35867.34	41484.72	41936.82	14557.74
CO_2 reduction by utilization (MT/yr)	24732.0	24732.0	24732.0	24732.0	24411.6	24411.6	-
Net CO_2 reduction; calculated from CO_2 emission from process – CO_2 reduction by utilization (MT/yr)	56037.87	29210.57	22201.38	11135.34	17073.12	17525.22	14557.74
CO_2 emission kg / kg of product DMC	1.2818	0.6681	0.5205	0.2512	0.4133	0.3760	0.5220
HTC / kg of product DMC	0.000306	0.000268	0.000251	0.000245	0.000454	0.000362	0.000493
GWP / kg of product DMC	3.5528	2.8504	2.6626	2.1138	4.2048	2.4448	1.808

LIST OF PUBLICATIONS

Kongpanna, P., Pavarajarn, V., Gani, R., & Assabumrungrat, S. (2015). Techno-economic evaluation of different CO_2-based processes for dimethyl carbonate production. *Chemical Engineering Research and Design, 93,* 496-510. doi: http://dx.doi.org/10.1016/j.cherd.2014.07.013

Frauzem, R., Kongpanna, K., Roh K.,, Lee, J.H., Pavarajarn, V,., Assabumrungrat, S., Gani, R., Chapter 7 – Sustainable Process Design: Sustainable Process Networks for Carbon Dioxide Conversion, Computer Aided Chemical Engineering.

Choomwattana, C., Chaianong, A., Kiatkittipong, W., Kongpanna, P., Assabumrungrat, S., Evaluation of Dimethyl Carbonate and Ethylene Glycol Production from Biomass, Computer Aided Chemical Engineering.

VITA

Pichayapan Kongpanna was born in Suratthani province, Thailand. Monday 21st November 1988.

After he finish high school "Suratthani School" in 2006, he wanted to be a soldier as his father and his cousin, dentist, pharmacist, computer engineer and chemical engineer. However, when he took an examination, he just passed only Engineering.

He started the engineering degree at Prince of Songkhla University. On the second year of engineering, He selected "Chemical Engineering" as 1st department and he studied in chemical engineering in 2007-2009. He attended petroleum summer school and joined Schlumberger as a student trainee for 1 month that motivated him to aim higher target for chemical engineering life. In 2008, he was a student trainee at Chevron at South Pailin department. After he graduated the bachelor degree in 2009. he contacted Prof. Suttichai for studying further in D.Eng.

After 3 years in Chulalongkorn University, he went to CAPEC-DTU for studying further in this research field. The computer aided tools and the systematic methodology were enlightened by his professor, Prof. Rafiqul Gani.

Finally, he came back from Denmark and working in CO2 utilization and conversion which based on simulation program to find the optimal solution for utilization of CO2.

Finally, for 6 years of Doctoral life, he learn a lot of knowledge from all great men. And Doctoral life give a lesson;

I was not born with whole lot of natural talent, not gifted but I work hard and I never give up.