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# Computer-Aided Sustainable Process Synthesis-Design and Analysis

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# COMPUTER-AIDED SUSTAINABLE PROCESS SYNTHESIS-DESIGN AND ANALYSIS

**Anjan Kumar Tula**
PhD Thesis
December 14th 2016

**DTU Chemical Engineering**
Department of Chemical and Biochemical Engineering

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PhD Thesis

**Anjan Kumar Tula**

Dec 14th, 2016

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This thesis has been submitted as partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Technical University of Denmark.

# ABSTRACT

Process synthesis involves the investigation of chemical reactions needed to produce the desired product, selection of the separation techniques needed for downstream processing, as well as taking decisions on sequencing the involved separation operations. For an effective, efficient and flexible design approach, what is needed is a systematic way to identify the types of tasks-operations that need to be performed, the corresponding design of the operation-equipment, their configuration, mass-energy flows, etc., giving an optimal flowsheet. Due to the fact that process synthesis problems are by nature combinatorial and open ended, a number of different solution approaches have been proposed. However the solution for any synthesis-design problem is dependent on the search space of alternatives and the process performance criteria which in most cases are influenced by economic factors. This work focuses on the development and application of a computer-aided framework for sustainable synthesis-design and analysis of process flowsheets by generating feasible alternatives covering the entire search space and includes analysis tools for sustainability, LCA and economics. The synthesis method is based on group contribution and a hybrid approach, where chemical process flowsheets are synthesized in the same way as atoms or groups of atoms are synthesized to form molecules in computer aided molecular design (CAMD) techniques. The building blocks in flowsheet synthesis problem are called as process-groups, which represent a single or set of unit operations that are selected by employing a thermodynamic insights based method. These building blocks are then combined using connectivity rules to generate all the feasible flowsheet alternatives. The main advantage of representing the flowsheet with process-groups is that, the performance of the entire process can be evaluated from the contributions of the individual process-groups towards the selected flowsheet property (for example, energy consumed). The developed flowsheet property models include energy consumption, carbon footprint, product recovery, product purity etc. In this way, the entire list of feasible chemical process flowsheets are quickly generated, screened and selected for further analysis. In the next stage, the design of the most promising process flowsheet candidates is performed through a reverse simulation approach, where the design parameters of the unit operations in the process flowsheet are calculated from selected process-groups definition. In the next stage the selected design is analyzed, for identifying process limitations or bottlenecks (hot-spots) using a comprehensive analysis method consisting of economic, life cycle and sustainability factors that are translated into design targets. In the final stage the identified hot-spots are targeted for overall process improvement and to generate innovative designs.

In this work the developed framework along with the associated methods and tools is tested through three case studies related to both chemical and biochemical industry in order to ascertain the applicability of the framework. In each of the cases numerous alternatives of novel and designs reported by others are quickly generated and evaluated. In all the case studies tested, the final design generated by the framework was novel and more sustainable.

# RESUMÉ PÅ DANSK

Processyntese involverer undersøgelse af kemiske reaktioner, der er nødvendige for at producere det ønskede produkt, udvælgelse af separationsteknikker nødvendige for downstream forarbejdning, samt beslutninger om sekvensering af de involverede separationsprocesser. For en effektiv og fleksibel designtilgang, er der behov for en systematisk måde at identificere de typer af opgaver og operationer, der skal udføres, den tilsvarende design af operation-udstyr, deres konfiguration, masse-energistrømme m.v., hvilket giver et optimalt processkema. På grund af det faktum, at processynteseproblemer er af natur kombinatoriske og med flere mulige løsninger, er der blevet foreslået en forskellige metoder til at overkomme dette. Men løsningen til ethvert syntese-design problem er afhængig af søgningsområdet af alternativer og kriterierne for procesydeevne, som i de fleste tilfælde er påvirket af økonomiske faktorer. Dette arbejde fokuserer på udvikling og anvendelse af et computerstøttet platform for bæredygtig syntese-design og analyse af processkemaer ved at generere mulige alternativer, der dækker hele søgningsområdet og omfatter analyseværktøjer for bæredygtighed, LCA og økonomi. Syntesemetoden er baseret på en gruppebidragsbaseret hybridmetode, hvor kemisk processkemaer syntetiseres på samme måde som atomer eller grupper af atomer syntetiseres til dannelse af molekyler i computerstøttet molekylært design (eng: CAMD) teknikker. Byggestenene i et processkemasyntese problem er betegnet som procesgrupper, som repræsenterer en enkelt eller et sæt af enhedsoperationer, der er udvalgt på metoder baseret på termodynamiske grundlag. Disse byggesten kombineres derefter under anvendelse af regler for tilslutningsmuligheder for at generere alle de mulige processkemaalternativer. Den største fordel ved at repræsentere processkemaer med procesgrupper er, at udførelsen af hele processen kan vurderes fra bidragene fra de enkelte procestrinsgrupper mod processkemaegenskaberne (f.eks forbrugt energi). De udviklede processkemaegenskabsmodeller omfatter energiforbrug, carbon footprint, produktudvinding, produktrenhed osv. På denne måde er hele listen over mulige kemiske processkemaer hurtigt genereret, screenet og udvalgt til yderligere analyse. I det næste trin, er udformningen af de mest lovende processkemakandidater udført gennem en omvendt simulationsmetode, hvor designparametre for enhedsoperationer i processkemaet er beregnet ud fra udvalgte definitioner af procesgrupper. I næste fase analyseres det valgte design, til at identificere begrænsninger eller flaskehalse (hot-spots) ved hjælp af en omfattende analysemetode bestående af økonomiske, livscyklus og bæredygtigheds faktorer, der omsættes til procesdesignmål. I den afsluttende fase identificeres hot-spotsne, som er målrettet til den samlede procesforbedring og til at skabe innovative designs.

I dette arbejde er den udviklede platform testet sammen med de tilhørende metoder og værktøjer gennem tre casestudier med relation til både kemiske og biokemiske industri med henblik på at fastslå anvendelsesmulighederne af platformen. I hvert af tilfældene er de mange alternativer og litteraturdesignene hurtigt genereret og evalueret. I alle de testede casestudier var de endelige designs, der genereres af platformen, nye og mere bæredygtige.

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I dedicate this thesis to four wonderful women of my life my mom, wife, sister and my daughter Akki.

Kgs Lyngby, December 2016

Anjan Kumar Tula

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# 1

# INTRODUCTION

Chemical flowsheet synthesis & design usually involves identification of the processing route to convert raw materials into desired product, investigation of chemical reactions needed, selection and design of the operations involved in the processing route, as well as calculations of utility requirements, the calculations of waste and emissions to the surroundings and many more. This is shown in Figure 1.While the flowsheet synthesis problem determines the sequence of the unit operations needed to achieve the conversion of the raw materials to desired products, flowsheet design problem determines the optimal conditions for equipment and process for the synthesized flowsheet. In chemical industry, process synthesis methods are not only applied to generate conceptual designs for new processes but also to retrofit problems where one seeks to improve the existing process. Due to increased emphasis by governments concerning environment, public health and safety through regulatory enforcements and growing competitiveness through globalization, the designed process have got to be sustainable and economically feasible solution for the synthesis problem. In general there are two common solution strategies to solve synthesis-design problems, simultaneous approach and decomposition based approach. In simultaneous approach, the synthesis problem is solved by considering all the constraints, components of the process synthesis simultaneously. On the other hand in sequential or decomposition approach the complexity of the synthesis problem is divided into set of sub problems that are solved sequentially in a predefined order.

In this chapter, first, the process synthesis problem is defined mathematically and explained. Second, an overview of state of art in process synthesis-design of chemical and biochemical processes is discussed in detail. Third, the project motivation and objectives behind this work are presented.

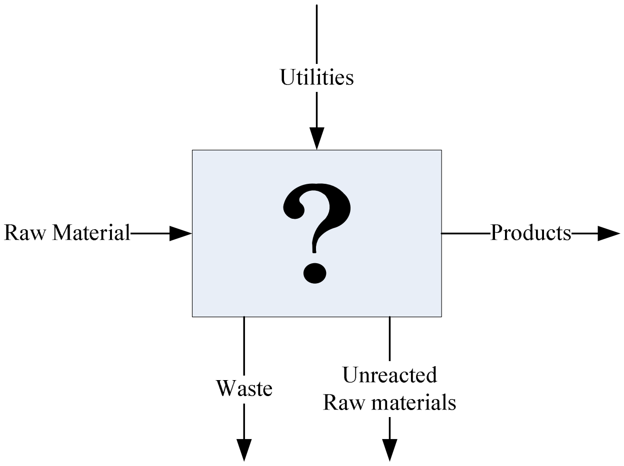


*Figure 1: Process synthesis problem*

## 1.1 GENERIC PROCESS SYNTHESIS PROBLEM DESCRIPTION:

In order to generate optimal process flowsheet structure & design, the synthesis-design problem has to be formulated and solved. The generic mathematical form of the synthesis-design problem can be represented as

$$\min/\max Z = f(x, y) \tag{1.1}$$

$$\text{s.t} \;\; h(x, y) = 0 \tag{1.2}$$

$$g(x, y) \leq 0 \tag{1.3}$$

$$x \in X, y \in \{0,1\} \tag{1.4}$$

Where the objective function $f(x, y)$ describes the performance of the process like capital/operational cost, energy consumed or profit which needs to be minimized or maximized. Equation 1.2 represents system of linear and/or non-linear equations such as the process model consisting of mass and energy balance equations and design constraints. While the constraints/specifications related to structure of the flowsheet are governed by equation 1.3, where x generally represents continuous variables like state or design variables and y represent discrete variables which takes values of (0,1) defining the selection of particular unit operation or action in the flowsheet structure. Several types of process design problems can be formulated as subset of the above equations. Due to the fact that process synthesis problems are by nature combinatorial and open ended, a number of different solution approaches have been proposed. These approaches can be broadly classified into three main classes of methods: methods that rely on knowledge base; methods that employ mathematical or optimization techniques; and, hybrid methods that combine different solution approaches into one method.

## 1.2 KNOWLEDGE BASED METHODS:

The most common school of thought to solve synthesis-design problems is to use knowledge based methods because of their ease of application and swift generation of a feasible solution to the defined problem. Knowledge based methods depend on information/rules, which are built over time from experience, various problem solving insights, engineering data and thumb rules to generate alternatives and propose a feasible alternative. These methods are generally applied on large problems to reduce the complexity of the synthesis problem. These methods often imply the evolution of the solution strategy of solving similar kind of problems. Even though knowledge based methods can quickly generate feasible process alternative for a synthesis problem, the optimality of the generated solution is not always guaranteed and will always depend on the information/data on which the method is built on. Knowledge based methods in general consists of three parts (Siirola and Rudd 1971; Nath and Motard 1981; Barnicki and Fair 1990; Jaksland, Gani, and Lien 1995).

- Data model: This is a structured framework in which available knowledge is organized.
- Data mining model: This model includes procedures to analyze and explore the data from the data model to extract relevant information which can be used for the current problem.
- Application model: In this model the extracted knowledge from the data mining step will be systematically transformed to rules/decision matrix which can be applied to the current problem.

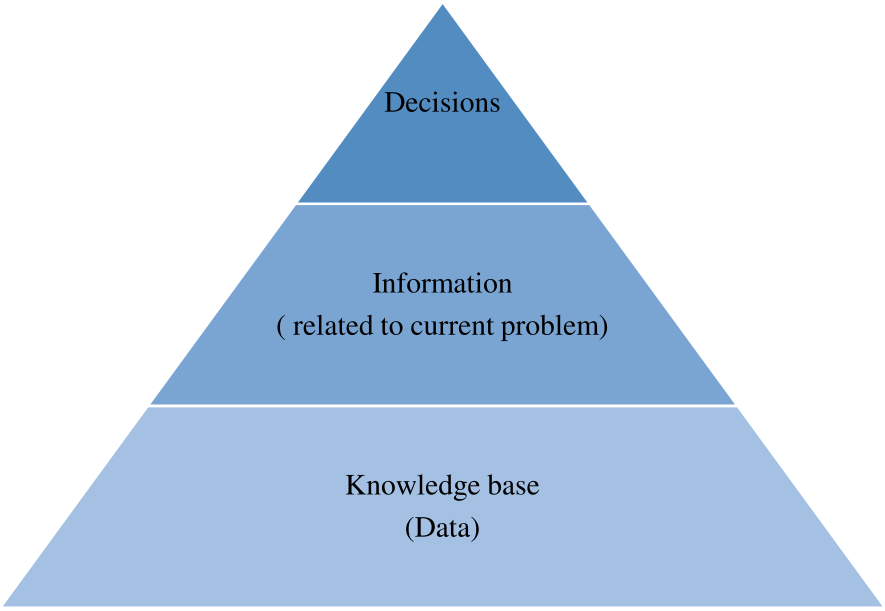


*Figure 2: Typical structure of knowledge based methods*

These methods in general mimics the human approach in solving the problem (Parmee 2005), where humans try to search the data to retrieve relevant information and decisions are made based upon the extracted wisdom to solve the problem. The major limitation with these methods are that sometimes the rules underlying these methods can become contradictory or conflicting or even overlapping in nature for specific problems so these methods along with the rules has to be carefully examined before applying. Knowledge base methods can be further divided into two groups based on the how the data mining model or the information related to current problem is generated.

### 1.2.1 Heuristics Based Methods:

Siirola, Powers and Rudd (1971) are one of the first researchers to propose a computerized process flowsheet generator based on heuristics to solve the synthesis problem. Siirola et al. tried to take advantage of the high-speed decision-making capabilities of the computer to automate the synthesis process and also on the other hand to explore a greater number of processing alternatives. Later Seader and Westerberg (1977) combined the heuristics based approach from Siirola et al. with evolutionary approaches (Stephanopoulos and Westerberg 1976) to propose a combined strategy for synthesis of simple separation systems. The main idea here is to generate an initial flowsheet based on heuristics and then systematically apply small changes to the original generated flowsheet based on evolutionary modification rules. The modified flowsheet is later verified with the original flowsheet using performance metrics. This combined approach was further expanded by Nath and Motard (1981) to include more evolutionary rules and also proposed a computer aided tool to synthesize multi component separations not only involving simple distillation columns but also separations involving mass separating agents. Nadgir and Liu (1983) later proposed an improved heuristic method by introducing rank ordered heuristics for systematic synthesis of initial sequences for multi component separations. These heuristics are classified into four categories: (1) Method heuristics (M heuristics) that favor certain separation methods; (2) Design heuristics (D heuristics) that favor separation sequences with specific desirable properties; (3) Species heuristics (S heuristics) that considers property differences between species to be separated; (4) Composition heuristics (C heuristics) that takes feed and product concentrations as a function of separation costs. Through this improved method Nadgir and Liu were able to solve different synthesis problems and were successful in generating better designs in terms of capital cost than the designs obtained using other methods. Newer heuristic methods often take the concepts of these original methods (Siirola, Powers, and Rudd 1971; Nath and Motard 1981), modify and convert them to use in a form of computer aided tool in process synthesis, and also expand the application range.

Most of the methods so far discussed are developed and applied for process synthesis involving sharp separations or high recovery systems, in which each component being separated appears in one and only one product stream. However, in most industrial processes, components simultaneously appear in two or more product streams. In regards to synthesis of separation systems involving sloppy separations Cheng and Liu (1988) proposed heuristics based method. In this method, Cheng and Liu developed a new way to represent the problem, called the component assignment diagram (CAD), in which different kinds of product configuration sets can easily be visualized. Further, they also proposed separation specification Table (SST) that is used in analysis for selecting different product splits. This method is extended further in the work by Liu et al. (1990) where a unified method was proposed to synthesize separations by all-sharp, all-sloppy and both sharp and sloppy separators. Also in this method, the CAD is expanded to a matrix form (CAM) to digitalize the information. Based on this approach of combined CAM with SST, an expert system called (PROLOG) was developed by Liu et al. (1990) for process synthesis. Barnicki and Fair (1990; 1992) also introduced a knowledge based expert system know as the separation synthesis advisor (SSAD), for separation synthesis of liquid mixuters and gas/vapor mixtures. The main idea here is to decompose the overall synthesis problem into series of independent sub tasks. Then the selector module in the knowledge based system selects the separation techniques for each task, based on pure component properties and on process characteristics.

Subsequently, Modi and Westerberg (1992) introduced the use of system information to develop the heuristics, rather than completely relying on the rules which are conflicting and overlapping. This method utilizes marginal price and the determining guiding point. This implements the same method as Gomez and Seader (1976) with an alternate predictor cost function. The marginal price is the price change that results when the separation is performed without nonkey components. Using Underwood's method, evaluation functions are developed that give some physical insight into the heuristics employed. The benefit of this method is that it can be applied to a variety of property models, allowing it to be applied to a variety of cases. In order to counter the conflicting nature of the rules used in heuristics methods Floquet et al. (1994) developed a fuzzy ruled based method for separation synthesis. In this method all the rules are converted systematically by quantifying all the subjective and qualitative terms ("large", "small"). One of the main limitations of heuristics methods is the application range of the method, which is limited to the process information available in the data model (Knowledge base). Pajula et al. (2001) tried to solve this limitation by introducing case-based reasoning (CBR) approach, which solves new problems by retrieving information from existing successful designs and adapting them to the needs of the new problem. This approach of case-based reasoning is further expanded for reactive separation processes by Avramenko and Kraslawski (2005).

Most of the methods so far dealt with synthesis of separation systems, But Douglas (1985) is one of the first researchers to propose a method based on hierarchical decomposition strategy for synthesis of entire chemical flowsheet. In this method, at each level in the hierarchy different decisions are made about the structure of the processing route based on heuristics. Douglas used process economics as criteria to select the better alternatives at different steps of his decomposition strategy. According to Douglas's hierarchical decomposition strategy, process synthesis has analysis of the process in 5 levels.

1. Batch vs. Continuous
2. Input-Output Structure
3. Recycle Structure and Reactor Considerations
4. Separation System Specification
    a. Vapor recovery
    b. Liquid recovery

5. Heat Exchanger Network

A similar method based on hierarchical decomposition strategy was proposed by Smith (2005), which defines a design starting from selection of reactors towards effluent treatment by adding layers of refinement. Figure 3 shows the representation of the hierarchical decomposition strategy proposed by Smith. Even though these methods allows for fast identification of a feasible configuration which is often located near optimal solution the main limitation of these methods lies in the impossibility of handling the interactions between different levels or layers in the hierarchy due to sequential nature of the approach.

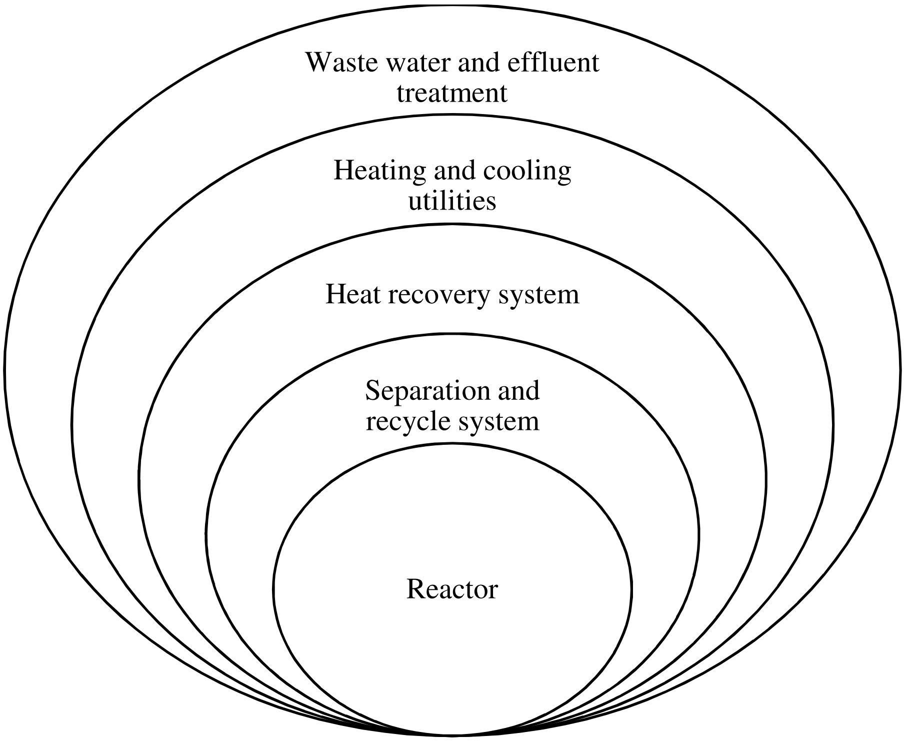


*Figure 3: Onion Diagram, Smith's representation for Process synthesis*

### 1.2.2 Thermodynamic Insights based methods:

These methods rely on thermodynamic information/ properties of the process rather than fixed rules to synthesize process configurations. One the for most researchers to propose a computer aided methodology based on relation between physio-chemical properties and the separation process principles is Jaksland et al. (Jaksland, Gani, and Lien 1995; Jaksland and Gani 1996). The methodology covers wide range of separation problems and includes identification of separation task and sequencing of feasible separation techniques. Most of the thermodynamic insight based methods proposed by the researchers (Tsirlin, Kazakov, and Romanova 2007; Tsirlin, Vyasileva, and Romanova 2009; Tsirlin and Sukin 2014; Bek-Pedersen and Gani 2004) are limited to synthesis of distillation column sequencing. But , Fox et al. (Fox et al. 2013; Sempuga et al. 2010) has proposed an method for synthesis of entire chemical process through graphical representation of the thermodynamic properties of the system. This method utilizes enthalpy (representative of process heat requirements) and Gibbs free energy (representative of work requirements) to synthesize process flowsheets that operate as close to reversibly as possible. With the visualization of the material, energy and work, it is possible to find the process that is as thermodynamically efficient as possible. With a thorough description of the elements of the graph, it is possible to use it for the design of entire process with thermodynamic considerations. The graphical method that is described using enthalpy and Gibbs free energy is applied to two case studies, gasification and production of syngas by steam reforming.

### 1.2.3 Mathematical optimization methods

Mathematical optimization methods are based on mathematical programming techniques using optimization to determine the best processing route from a superstructure of alternatives. These methods has three important steps:

- In the first step, a superstructure of all the alternatives for the given synthesis problem is setup.
- The second step is to formulate the mathematical problem involving the superstructure of alternatives.
- In the last step the formulated mathematical problem will be solved using suitable solution strategies to generate the optimal processing structure.

The superstructure in this case represents a network of all possible alternatives where all possible connections between unit operations are considered through decision variables and structural design parameters. Initially mathematical optimization or superstructure based optimization methods has been successfully applied to synthesize homogenous subsystems (Floudas, Ciric, and Grossmann 1986; Yee and Grossmann 1990; Kokossis and Floudas 1990; Kokossis and Floudas 1994; Esposito and Floudas 2000) like sequencing of distillation columns, optimization of reactor and heat exchanger networks. In synthesis of distillation column sequencing research was carried on both sharp and sloppy separations. In applying optimization methods to heat exchanger networks, alternatives are generated from the development of the superstructures representing heat exchanger networks. The objective functions particularly used for HEN synthesis extended beyond the minimization of utilities/cost associated to operability of the HEN (Papalexandri and Pistikopoulos 1996). Since the introduction of this approach for complete process synthesis, various solution strategies and optimization techniques are proposed to solve the resulting Mixed Integer Non-linear Programming (MINLP) problem to obtain optimal processing route. Duran & Grossmann (1986) were the first researchers to propose Outer-Approximation (OA) algorithm for solving Mixed Integer Non-linear Programming (MINLP) problems.

In general the Outer-Approximation algorithm consists of two parts; the first part is considered as Non-linear Programming (NLP) sub problem when the initial continuous variables for a specific flowsheet structure are optimized and the rest of process flowsheet alternatives are then sub optimized for the given flow; in the second part, an Mixed Integer Linear programming (MILP) master problem is obtained for generating new candidate flowsheet configurations in order to determine an optimal configuration. However the algorithm doesn’t guarantee a global optimal solution when applied to a non-convex problem. Later Kocis and Grossmann (1987;1989) modified the algorithm and effectively addressed the MINLP optimization of processs flowsheet configurations by introducing the

Modeling/Decomposition (M/D) strategy and the synthesis problem was solved using Outer Approximation with Equality Relaxation (OA/ER) algorithm. The technique exploits the separability of the MINLP for process superstructure by partitioning the superstructure into nodes for process units and interconnection units. Raman and Grossmann (1994) introduced the Generalized Disjunctive Programming (GDP) modeling framework as an alternative representation of mixed integer programming which later this algorithm has been implemented to solve the process synthesis flowsheet problems. In this framework Raman and Grossmann addressed the issue of modelling discrete programming problems with the use of logical disjunctions and propositional logic. The authors also demonstrated the efficacy of the method by solving process networks and scheduling problems. An extensive review on MILP and MINLP techniques can be found in Johnson et al. (Johnson, Nemhauser, and Savelsbergh 2000) and Grossmann (1990; 2002). Most of the mathematical programming methods so far discussed for synthesis of entire flowsheet are always limited by the flowsheet patterns that follow more or less the hierarchical decomposition strategy. In order to overcome this Papalexandri and Pistikopoulos (1996) introduced a general modelling framework for process flowsheet synthesis based on mass/heat principles. A mass/heat transfer block which characterized by mass/heat transfer phenomena was embedded in the superstructure to represent the entire process flowsheets and the problem was formulated as MINLP model.

Later Yeomans and Grossmann (1999) suggested a systematic modeling framework for process synthesis problems that relies on two different types of superstructure representations; State Task Network (STN), in which the process tasks and states must be specified while the process unit is unknown and State Equipment Network (SEN), which states of the process and process units are identified first, then different process tasks that each process unit can implement must be determined. They solved the flowsheet process synthesis problem through Generalized Disjunctive Programming (GDP) in order to understand the relationship between modeling, STN and SEN representations. The GDP is then reformulated into MILP or MINLP problems in a systematic way in order to solve the synthesis problem. Türkay and Grossmann (1996) presented logic-based MINLP algorithms for problem formulation of network synthesis problems with the GDP. Later, the authors proposed two levels of discrete decisions to solve synthesis of process flowsheet problem. In this GDP algorithm, it consists of MINLP sub problems for the fixed process flowsheet structures, which obtained with the convex hull reformulation and MILP master problems to predict new process flowsheets. In retrofitting cases, Jackson & Grossmann (2002) offered an optimization strategy using multiperiod generalized disjunctive programming (GDP) model for evaluating a complete process network at a higher level and analyzing a detailed process flowsheet at a lower level.

Mathematical optimization methods were further expanded to include simultaneous optimization of process topology, with utility networks and also water networks. It was first Duran and Grossmann (1986a) who proposed a solution strategy for simultaneously handling of heat integration problem while optimizing the process topology by formulating a nonlinear programming model with a set of constraints based on a pinch method to predict the minimum utility requirements. Later, Lang et al. (1988) implemented the model developed by Duran and Grossmann (1986a) to solve the simultaneous optimization of heat integration of the process flowsheet with sequential modular simulators. In another work, Yee et al.(1990)

incorporated the heat integration into the process model by setting the NLP and MINLP constraints where the specification of a heat recovery approach temperature (HRAT) is not required. A simultaneous optimization of water, heat and flowsheet was proposed by Yang and Grossmann (2013) where an LP targeting model is developed to predict tight upper bounds which combined with heat targeting model into process flowsheet optimization in order to obtain the best operating conditions.

Quaglia et al. (2012) proposed a systematic framework for synthesis of processing networks by integrating business and engineering aspects. The proposed framework comprises of different methods and tools needed in order to define and formulate problem as a MINLP. The stage-wise superstructure representation presented in this work has a similarity with the stage-wise superstructure for heat exchanger networks problem developed by Yee et al.(1990). Here a superstructure representation considers all possible processing routes and technological alternatives in order to transform potential feedstock's to products. The technological alternative is represented as process interval that comprises of various process tasks. A generic process interval model developed in the framework was adapted and modified from a previous study dealing with bio-refinery processing network by Zondervan et al. (2011) by adding waste separation task in the process interval.

The main advantage of using mathematical optimization for process synthesis is that since optimization of both process topology and process conditions are done in simultaneous approach all the component interactions are considered while solving the problem. However the major limitations of this approach are that the solution of the synthesis problem heavily depends on the superstructure of the alternatives considered. So in order to find the optimal process topology for a given synthesis problem, the original search space should constitute the optimal pathway. Also since the process synthesis problem is by default non linear in nature, the solution to such optimization problem is difficult.

## 1.3 HYBRID METHODS:

Since application of knowledge based methods do not guarantee optimality for a given flowsheet synthesis problem while mathematical (structural optimization) techniques are limited by availability and application range, many researchers proposed Hybrid methods, which combine different approaches into one to solve the synthesis problem. These methods concentrate on narrowing the search space in order to reduce the size of the synthesis problem and to obtain near-optimal solutions which deserve to be analyzed in more detail.

Lu and Motard (1985) were one of the first researchers to propose a hybrid method based on linear programming and evolutionary principles to synthesize complete flowsheets. The method starts with generating a preliminary process flowsheet by solving the stream matching problem involving raw materials and desired products matrices using successive linear programming techniques. Then the separation tasks in the preliminary flowsheet are synthesized using set of heuristics and the flowsheet is further improved by applying evolutionary rules. While Lu and Motard's method combines mathematical programming with heuristics to solve the synthesis problem, Fonyo and Mizsey (1990; 1986) introduced a framework that utilizes hierarchical decomposition and mathematical optimization methods. In this methodology preliminary designs are generated using hierarchical decomposition methods and are screened initially with shortcut models for energy and total costs. These generated designs are later verified with respect to user-driven additional implicit knowledge like complex configurations, constraints etc. and finally solved using algorithmic methods. Fonyo and Mizsey also showed that the proposed method will be able to solve the integrated process synthesis and heat exchanger network problem.

While most of the methods discussed above were developed to synthesize of organic chemicals, Steffens et al. (2000) were one the first group to introduce a hybrid method to synthesize bioprocesses. Steffens integrated physical property information of the chemical species present in the synthesis definition with implicit enumeration methods to solve the synthesis problem. Physical property information is used to screen and reduce the search space of unit operations feasible for the given problem. Later this synthesis MINLP problem is solved by discrete programming by translating the continuous variables into discrete values. Steffens et al. illustrated the synthesis framework through two case studies: the generation of process flowsheet candidates for the downstream purification process for a protein secreted from S. cerevisae and for the purification of an animal growth hormone bovine somatotropin (BST).

Later along similar lines Hostrup and Gani (Hostrup et al. 2001) proposed full-fledged integrated method based on thermodynamic insights and mathematical programming for process synthesis and design problems. This method consists of three main steps, Pre-analysis, Flowsheet and superstructure generation, Simulation and optimization. In this method thermodynamic insights are used to generate processing alternatives, which are used to define the superstructure for the flowsheet optimization problem. The optimal flowsheet is then determined by solving the resulting structural optimization problem through a suitable MINLP model. Finally the method comprises of a validation step, where a simulation engine is used to verify the design generated by the method.

Rigopoulos & Linke (2002) has applied a stochastic optimization-based synthesis framework for reaction/separation networks to synthesis of waste water treatment network. The framework consists of two basic elements: a) a general modeling framework to account for all possible design options in form of a superstructure model (includes generic synthesis units and interconnecting streams), and b) an optimization framework to systematically search the solution space defined by the superstructure in order to identify targets of maximal performance and a set of designs that exhibit near target performances. Later Li et al. (2003) proposed a combined method for process synthesis with waste minimization which involves conflict based analysis and mathematical programming. The method is based on a three –step hierarchical approach for generation of process alternatives, in the first step the waste sources are identified through problem analysis. In second step, suitable heuristics or techniques are selected in order to improve the concerned characteristics that are related to waste sources. Based upon these techniques various pollution prevention alternatives are generated which serves as the superstructure aimed at waste minimization. In the last step the resulting optimization problem is solved using suitable MINLP model.

d'Anterroches & Gani (2005) developed a framework for computer aided flowsheet design (CAFD) based on principles of the group-contribution approach in chemical property estimation . In this method process flowsheets are synthesized in the same way as atoms or groups of atoms are synthesized to form molecules in computer aided molecular design (CAMD) techniques. The fundamental pillars of this framework are the definition and use of functional process-groups (building blocks) representing a wide range of process operations, flowsheet connectivity rules to join the process-groups to generate all the feasible flowsheet alternatives and flowsheet property models to evaluate the performance of the generated alternatives.

## 1.4 PROJECT MOTIVATION AND OBJECTIVES:

From the review of current state of art in process-synthesis-design, it is clear that most of the methods so far developed can be categorized either as knowledge based approaches, mathematical optimization approaches or hybrid approaches. Since applying only knowledge based methods or optimization based methods often over simplify or complicates the process synthesis problem, the more logical way is to combine two or more approaches to develop a hybrid method to solve the synthesis problem. And also from the literature review, most of the methods developed so far lack comprehensive analysis/consideration of sustainability in early stages of process synthesis, which could lead to a process alternative that is feasible but not sustainable. Therefore, this work focuses on integration of different approaches and tools into a systematic synthesis-design and analysis framework to solve the synthesis and design problem. This work is also focused on introducing various analysis methods related to sustainability and life cycle assessments during selection of process alternatives.

The main objectives of this PhD thesis are as follows:

1. To develop computer-aided framework for sustainable synthesis-design and analysis of process flowsheets for both chemical and biochemical processes that is capable of generating feasible alternatives covering the entire search space for any given synthesis problem.
2. Development of method which is capable of evaluating the generated alternatives quickly and efficiently without using rigorous models.
3. Use of sustainability, economic and life cycle analysis in early stages of process synthesis-design of flowsheets to generate more sustainable and energy efficient designs.
4. Integration of methods and tools for simultaneous optimization of process and heat exchanger network.
5. Development of method for synthesis and design of innovative alternatives consisting of hybrid separations.
6. Development of software architecture and implementation of the developed framework as a computer-aided tool for sustainable process synthesis-design.

## 1.5 THESIS STRUCTURE:

This thesis has 6 chapters and the outline of the each chapter is as follows:

In chapter 1, the process synthesis-design problem is defined and the generic mathematical representation of the same is explained in detail. Detailed literature review of the current approaches and associated methods to solve the synthesis problem are highlighted. Finally the project motivation along with objectives of the project which this thesis seeks to address is given.

In chapter 2, important definitions that are used in this work are explained along with the core concepts and highlight the theories that support the method developed in this thesis.

In chapter 3, a complete overview of the developed framework for sustainable process synthesis-design is given. The detailed work-flow and data-flow implemented in the methodology are presented systematically, that is, the calculations performed, the methods applied and the corresponding tools used for, each step in the framework are explained in detail.

In chapter 4, the implementation of the developed method as a computer-aided tool is described. The high level architecture of the tool along with corresponding algorithms associated with each step of the framework is given.

In chapter 5, application examples used to test the developed method for sustainable process synthesis-design are presented. Three case studies are chosen to highlight different aspects of the developed method. The first example deals with production of benzene from toluene while the second example is related to production of bioethanol from lignocelulostic material. The final example is related to separation of alkane isomers, where the synthesis and design of innovative solutions are highlighted.

Chapter 6 outlines the main achievements of this work and also provides future perceptive and directions for further expansion/improvement of the framework.

# 2

# DEFINITIONS AND CONCEPTS

In this chapter, the definitions of different terms used in various stages of the developed methodology are presented and explained. Then, all the concepts and theories that are used in this work are explained in detail. Methods based on these concepts are later used in various stages of the sustainable synthesis methodology.

## 2.1 DEFINITIONS

**Process Topology**: Flowsheet structure representing a process as an ensemble of unit operations and their connections.

**SFILES:** An acronym for "Simplified Flowsheet Input Line Entry System," which is a ASCII string that stores the process topology of generated process alternatives, similar to SMILES for chemical structures.

**Flowsheet Property Model**: These models represent different performance metrics that can be used to evaluate the overall performance of the entire flowsheet. These performance metrics are expressed as sum of contributions of the each process-groups present in the flowsheet.

**Retrofit Problem**: This represents a form of synthesis problem, where one seeks to find design alternatives for a unit operation or set of unit operations keeping remaining unit operations (flowsheet structure) fixed. This is a common practice when the process already exists (has been build) and modifications are desired.

**Binary Ratio Matrix**: This matrix represents the property differences of all the binary pairs of components present in the synthesis problem as their property ratios. For example, the ratio of melting points for a binary pair.

**Sustainable Process Design**: The objective of sustainable process design is to generate processing alternatives that have better/improved economic, environmental and life cycle analysis factors.

## 2.2 CONCEPTS:

### 2.2.1 Identification of Feasible Separation Techniques:

Process synthesis involves generating the downstream separation network for a multicomponent mixture to produce the constituent product streams or/and recycle streams. In addition, for each separation task involved in the downstream separation, more than one separation technique is feasible. In order to find best processing route for a given raw material to products it is imperative to consider all the separation techniques that are feasible for each of the identified separation tasks in the synthesis problem. Since all the separation techniques exploit physiochemical property differences between the separating components, a comprehensive and systematic analysis of physical and chemical properties of the mixture components to be separated will result in identification of all feasible separation techniques. Jaksland et al. (1995) propose a method which identifies feasible separation techniques based on analysis of pure component and mixture properties of the mixture to be separated. Table 1 gives the important properties of the separating mixture that are to be considered for each of the separation technique.

*Table 1: Properties related to each Separation Techniques*

| **Separation Technique** | **Separation Type** | **Important pure component properties** |
|---|---|---|
| Absorption | Gas separation | Solubility parameter |
| Azeotropic distillation | Vapor-liquid separation | Vapor pressure, formation of azeotropes, solubility parameter |
| Cryogenic distillation | Vapor-liquid separation | Vapor pressure, heat of vaporization, boiling point |
| Crystallization | Solid-liquid separation | Melting point, heat of fusion at melting point |
| Desublimation | Vapor-liquid separation | Triple point (temperature and/or pressure) |
| Distillation | Vapor-liquid separation | Vapor pressure, heat of vaporization, boiling point |
| Drying | Solid-liquid separation | vapor pressure, diffusivity |
| Extractive distillation | Vapor-liquid separation | Vapor pressure, heat of vaporization, boiling point, solubility parameter |
| Flash Operation | Vapor-liquid separation | Vapor pressure, heat of vaporization, boiling point, surface tension |
| Foam fractionation | Liquid separation | Surface tension |
| Gas separation membranes | Gas separation | Critical temperature, van der Waals volume |

| | | |
|---|---|---|
| Ion exchange | Liquid separation | Ion charge |
| Leaching (solid-liquid extraction) | Solid-liquid separation | Solubility parameter, diffusivity |
| Liquid-liquid extraction | Liquid-liquid separation | Solubility parameter |
| Liquid membranes | Liquid separation, Gas separation | Solubility parameter, molar volume, radius of gyration, affinity to carrier |
| Microfiltration | Liquid separation | Size, molecular weight |
| Molecular sieve adsorption | Gas separation, Liquid separation | Kinetic diameter, van der Waals volume, polarizability, dipole moment |
| Partial condensation | Vapor-liquid separation | Vapor pressure, heat of vaporization, boiling point |
| Pervaporation | Liquid-vapor separation | Molar volume, solubility parameter, dipole moment |
| Stripping | Gas-liquid separation | Solubility parameter |
| Sublimation | Solid-vapor separation | Triple point (temperature and/or pressure) |
| Supercritical extraction | Liquid-liquid separation | Solubility parameter, critical temperature, critical pressure |
| Ultrafiltraion | Liquid separation | Size, molecular weight |

Jaksland et al. also propose the generation of binary ratio matrix, where the property differences between all binary pairs are represented in terms of property ratios to select the feasible separation techniques when the property ratios is greater than a certial threshold value (refer Table H1 from Appendix H for list of threshold values used for each separation technique). The binary ratio matrix for a multicomponent mixture of NC components has NB binary pairs, which is given by the Equation 2.1.

$$NB = \frac{NC(NC-1)}{2} \tag{2.1}$$

The binary ratio for each identified binary pair is calculated using Equation 2.2. Here the binary ratio of a property is always >1 because it is calculated by placing the property with the lower value in the denominator.

$$r_{ij} = \frac{P_{Aj}}{P_{Bj}} \tag{2.2}$$

Where $r_{ij}$ is the binary ratio and P is the pure component property for compound A and B.

**Conceptual example**: Consider a 3-component mixture comprising methanol, water and ethanol to be separated. Four pure components properties of the three components are given in Table 2.

*Table 2: Pure component properties for the 3-component mixture*

| | **Boiling point** (K) | **Radius of gyration** (nm) | **melting point** (K) | **molar volume** ($m^3$/kmol) |
|---|---|---|---|---|
| Methanol | 337.9 | 1.6 | 175.5 | 4.1E-02 |
| Ethanol | 351.4 | 2.3 | 159.1 | 5.9E-02 |
| Water | 373.2 | 0.6 | 273.2 | 1.8E-02 |

Using Equation 2.1, the total number of binary pairs for the system will be three. The binary ratio matrix is constructed for the identified three binary pairs for the selected properties using the Equation 2.2 and Table 3 gives the resultant binary ratio matrix for the system.

*Table 3: Binary ratio matrix for the 3-component system*

| | | **Boiling point** | **Radius of gyration** | **Melting point** | **Molar volume** |
|---|---|---|---|---|---|
| Methanol | Ethanol | 1.04 | 1.46 | 1.1 | 1.44 |
| Methanol | Water | 1.1 | 2.52 | 1.56 | 2.25 |
| Water | Ethanol | 1.06 | 3.67 | 1.72 | 3.24 |

## 2.2.2 Process-groups:

The process-group concept introduced by d'Anterroches & Gani (2005) applies the principles of the group contribution approach used for chemical property estimation to the synthesis and design of chemical and biochemical processes (Alvarado-Morales et al. 2010; Bommareddy, Chemmangattuvalappil, and Eden 2012; Tula, Eden, and Gani 2015). In a group contribution method for estimating pure component/mixture properties of a molecule, the molecular identity is described by means of a set of functional groups of atoms bonded together to form a molecular structure. Once the molecular chemical structure is uniquely represented by the functional groups, the specific properties can be estimated from regressed contributions of the functional groups representing the molecule. Having the groups, their contributions and their interactions, together with the governing rules on how to combine the groups into a molecule, enables the synthesis of molecules and/or mixtures. This is known as CAMD, computer aided molecular design. Similarly, each group used to represent a fraction of a molecule can be extended to represent a chemical process operation or a set of operations in a chemical process flowsheet. A functional process-group represents either a unit operation (such as a reactor, a distillation column, or a flash) or a set of unit operations (such as two distillation columns in extractive distillation, or pressure swing distillation). The bonds between the process-groups represent the streams connecting the unit operations, similar to the bonds combining (molecular) functional groups. Just as CAMD applies connectivity rules to combine the molecular functional groups to form feasible molecular structures, functional process-groups have connectivity rules to combine process-groups to form structurally feasible process alternatives. Finally, with flowsheet property models and corresponding process-group contributions, it is possible to predict various flowsheet properties, which can be used as performance indicators for screening of alternatives. For example, in Figure 4, a simple process flowsheet composed of a reactor, flash column, distillation and membrane separation process, in that order, can be represented with process-groups.

Consider the process flowsheet in Figure 4. The feed streams to the reactor can be represented by two process-groups; one inlet process-group (iA) for reactant A, and an inlet process-group (iB) for reactant B. Similarly, products are represented by two outlet process-groups: (oC) and (oD). The reactor process-group is (rAB/ABCD), which shows that the reactor has one inlet and one outlet. The process-groups representing a flash and a distillation are (flA/BCD) and (dlCD/B), respectively, represent that these units have one inlet and two outlets. Finally, the membrane separator is represented by a membrane process-group (gmC/D). From the list of process-groups available, a feasible flowsheet structure can be created as shown in Figure 4.

As in group contribution based molecular property prediction (where the same molecular groups may be used to represent many molecules), the same process-groups with different chemical species can also be used to represent different tasks in the flowsheet, as long as the property of the task matches. This makes the process-groups property dependent but not chemical species dependent. Therefore, the use of the same process-groups to represent different chemical species having similar properties is also valid in the case of process flowsheets. Note, however, that the inlet and outlet streams (bonds/connections) of process-groups must maintain the list of components present in them and that the path of a component through a process-group establishes the flowsheet structure. That is, process-groups (*A/BC*) and (*B/C*) can be connected to form [-(*A/BC*)-(*B/C*)-] without knowing the identities of the components *A*, *B*, and *C*. The identities of the chemicals (components) are only needed when the properties of the flowsheet need to be calculated. Table 4 represents the available process-groups along with their corresponding unit operations.

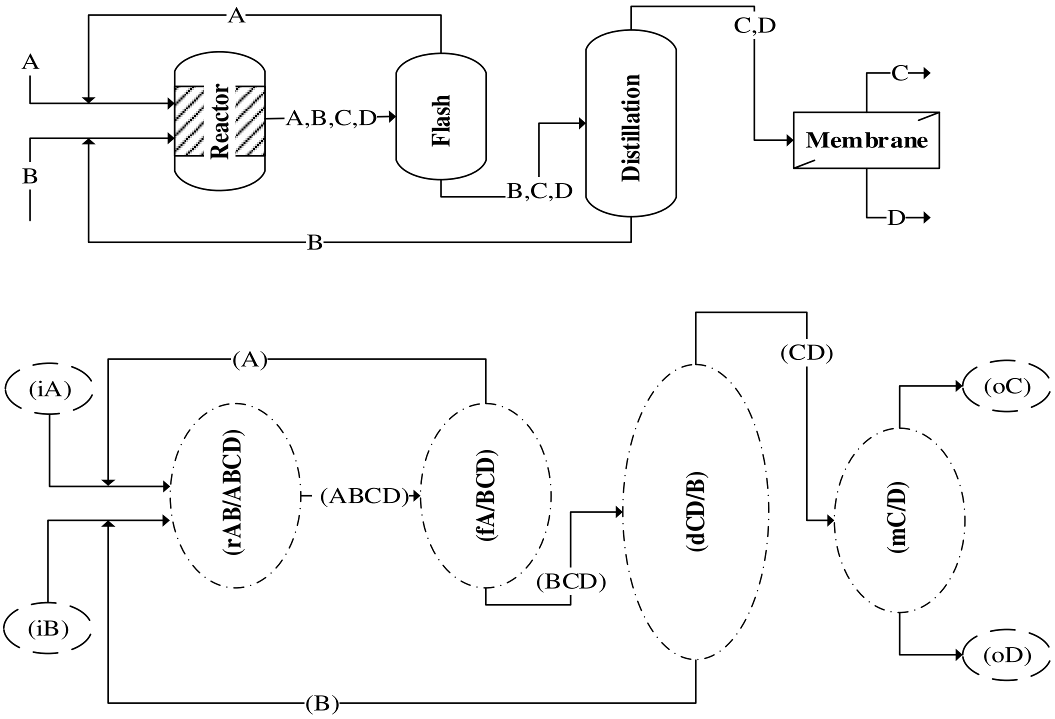


*Figure 4: Process-group representation of a chemical process flowsheet.*

*Table 4: Process-Groups representing different unit operation/s*

| **Representation** | **Process-Groups** | **Unit operation** |
|---|---|---|
| (dlA/B),(dlAB/C) | Distillation column | Simple distillation |
| (edA/B) | Solvent based extractive distillation | Extractive distillation |
| (azA/B) | Solvent based azeotropic distillation | Azeotropic distillation |
| (llA/B),(llAB/C) | Solvent based liq-liq extraction | Liq-Liq extraction |
| (psA/B) | Pressure swing distillation | Low and high press columns |
| (flA/B) | Flash | Flash operation |
| (dcA/B) | Filtration, decantation | Solid liq separation |
| (msA/B) | Molecular sieve separation | Molecular sieve |
| (pvB/C) | Pervaporation based separation | Pervaporation |
| (lmA/B) | Liq membrane based separation | membrane |
| (gmA/B) | gas membrane based separation | membrane |
| (laA/B) | Liquid Adsorption based separation | Adsorption |
| (gaA/B) | gas Adsorption based separation | Adsorption |
| (czA/B) | Crystallization based separation | Crystallization |
| (rxABC/ABCDE) | Kinetic, conversion based reactors | Reactors |
| (iA),(iAB) | Inlet streams | - |
| (oA),(oAB) | Outlet streams | - |

#### 2.2.2.1 Initialization of Process-groups:

Once the process-groups are identified, based on the feasible separation techniques, the selected process-group can be initialized with different sets of components. This can be done if each set is matching the property dependence of the process-group.

For example, consider a mixture of five components labeled as A, B, C, D, and E in the synthesis problem. Based on boiling point ratios, a feasible separation task is identified between components B and C. The corresponding separation technique associated with this set of properties is distillation and the process-group representing this separation technique is the distillation separation process-group. Therefore, the distillation process-group can be initialized with four different sets of components as shown in Table 5. This is based on the assumption of an ideal system, where no binary azeotropes exist, and assuming that the components are ordered according to decreasing relative volatility. Once the process-groups are initialized with all possible component combinations, they are added to the pool of process-groups to be used in the synthesis algorithm to generate the process flowsheets.

*Table 5: Initialization of a distillation process-group with a 5-components synthesis problem*

| **Components in the synthesis problem** | A, B, C, D, E | | | |
|---|---|---|---|---|
| **Separation task** | B/C | | | |
| **Property dependence** | Boiling point | | | |
| **Separation technique** | Distillation separation between B & C | | | |
| | **2** | **3** | **4** | **5** |
| **Matching set of components** | (BC) | (ABC) | (ABCD) | (ABCDE) |
| | | (BCD) | (BCDE) | |
| **Process-groups initialized** | (dlB/C) | (dlAB/C) | (dlAB/CD) | (dlAB/CDE) |
| | | (dlB/CD) | (dlB/CDE) | |

### 2.2.2.2 Generation of Flowsheet from Process-groups:

Since the concept of process-groups is similar to functional groups in computer-aided molecular design problem, the algorithms used to generate feasible molecular structures in CAMD approach can be used to generate flowsheet alternatives from process-groups. The generate and test approach proposed by Harper et.al (1999) to generate all feasible molecular structures from the selected functional groups, can be applied in the case of process-groups to generate feasible flowsheet structures. The main advantage of this approach is that the synthesis of alternatives (molecular structures) is decoupled from the evaluation with respect to the target properties. This provides the possibility to generate a large number of molecular structure alternatives and a fast evaluation of the property targets, while having the precision and the range of application of a group contribution method. In order to avoid the problem of combinatorial explosion generally associated with CAMD algorithms (enumeration), a set of connectivity rules are formulated, which are defined based on the structural and logical feasibility of the process flowsheet.

**Connectivity rules for generation of flowsheet using process-groups:**

1. The flowsheet starts with inlet process-groups and process-groups are added systematically until all defined outlet process-groups are achieved. Process-groups are combined or added based on the following rules. The rules are explained using an example of distillation process-group, which separates a four compound mixture (ABCD) into two streams of (AB) and (CD).
2. Only process-groups which have all the set of components (ABCD) to be processed by the distillation process-group can precede (can come before) the distillation process group (dlAB/CD).

   a. For example: one input process group defined as iABCD or a process group with components (ABCD) as output such as (rAB/ABCD) can serve as input to the process group (dlAB/CD).

3. Only process groups matching the set of components for each output of the process group (dlAB/CD) can be structurally combined with the distillation process-group.
   a. There are three possible combinations: two output process groups defined as (oAB) and (oCD), one output process group defined as (oAB) and one separation process group such as (gmC/D) and two separation process-groups defined as (lmA/B) and (czC/D).
4. Process-groups representing, unreacted raw material streams are by default sent back or connected to reactor with a purge.
5. Two-phase reactor process-group is always followed by a flash process-group.

Apart from satisfying structural connectivity, as elaborated above, combining two process groups should also follow the logical rules related to feed conditions and operational temperature limits as shown in Table 6.

*Table 6: Logical rules with respect to feed conditions for different process-groups*

| **Process-groups** | **Feed conditions** | **Operating temperature** |
|---|---|---|
| Gas membrane PG | V | <50˚C |
| Liquid Membrane PG | L | <50 ˚C |
| Distillation PG | V, L,VL | |
| Molecular sieve PG | L | <100 ˚C |
| Crystallization PG | L | >0 ˚C |
| Absorption PG | V, L | |
| PS Distillation PG | V, L,VL | |

Following these connectivity rules and based on the definition of each process-group in the flowsheet structure, it is ensured that the generated flowsheet topology represents a feasible flowsheet for the defined problem.

**Conceptual example to highlight the importance of connectivity rules:**

Consider a 4-component mixture to be separated into its constituent product streams. Table 7 gives the identified process-groups for the given problem. Here process-group “iABCD” represents the feed stream and the process-groups “oA”, “oB”, “oC” and “oD” are the desired product streams. While other process-groups represent the separation process-groups to achieve the product streams.

*Table 7: Process-groups selected for 4-component separation synthesis problem*

| **Process-groups** | | | | |
|---|---|---|---|---|
| iABCD | dlAB/CD | msABC/D | abA/BC | lmA/B |
| oA | msAB/CD | czA/BCD | dlA/BC | gmA/B |
| oB | abAB/CD | lmA/BCD | czBC/D | msA/B |
| oC | dlABC/D | dlA/BCD | dlBC/D | dlB/C |
| oD | gmABC/D | lmA/BC | msBC/D | dlC/D |

In order to separate 4-component mixture into four product streams, the minimum number of separation tasks needed is given by the equation 2.3.

$$N_{ST} = NP - 1 \tag{2.3}$$

Where NP is the number of product streams and $N_{st}$ is the number of minimum separation tasks required.

The total number of possible process-group combinations/flowsheets available can be calculated by equation 2.4.

$$\text{Total Flowsheets} = \frac{n!}{r!(n-r)!} \tag{2.4}$$

Where n is the number of available process-groups and r represents the minimum number of separation tasks identified using equation 2.3.

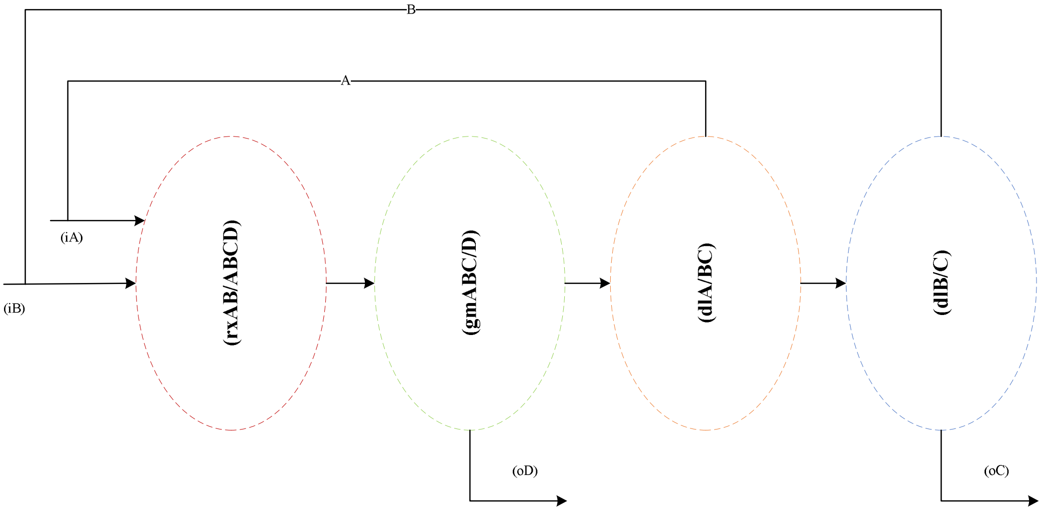
Table 8 gives the statistics for the number of flowsheets that are generated with and without using the connectivity rules. While the total number of possible combinations available are 1140, by applying the connectivity rules, the total number of feasible alternatives that are generated for the given synthesis problem is only 27. For the complete list of generated alternatives, refer Table G1 of Appendix G.

*Table 8: Statistics for given synthesis problem of a 4-comonent mixture*

| **Statitics** | |
|---|---|
| Number of separation process-groups | 20 |
| Number of inlet/outlet process-groups | 5 |
| Number of alternatives possible | 1140 |
| Number of feasible alternatives generated | 27 |

### 2.2.2.3 SFILES representation of Flowsheet:

Using the concept of process-groups and the physical insights-based method to identify all feasible separation techniques, there is the possibility to generate a large number of feasible process alternatives. Therefore, in order to efficiently store, retrieve and manuplate information of process alternatives, the process topology of the alternatives can be stored smartly in an ASCII format. This concept is called SFILES (Simplified Flowsheet Input Line Entry System), and was introduced by d'Anterroches and Gani (2006) to store the structural information of process flowsheets. The SFILES concept for flowsheets is similar to SMILES (Simplified Molecular Input Line Entry System) developed by Weininger (1988). SMILES are a form of line notations for describing the structure of chemical molecules using short ASCII strings. On similar lines, a process flowsheet can also be represented using and ASCII string. Figure 5 gives the SFILES string of a simple flowsheet structure represented by process-groups.



- (iA)(rxAB/ABCD)<1<2[(iB)](gmABC/D)[(oD)](dlA/BC)1(dlB/C)2(oC)

*Figure 5: SFILE representation of process alternative*

SFILES, similar to SMILES, are read from left to right. The process-groups representing specific tasks in the flowsheet are delimited by parenthesis. For example, in Figure 5 the membrane separation task is represented by (gmABC/D) in the given flowsheet SFILE. Two consecutive process-groups represent a connection from the first process-group to the second process-group. For example, (iA) (rxAB/ABCD) represents an inlet process-group connected to a reactor process-group. In the SFILES notation, branches are represented by square brackets and recycles are represented by using numbers similar to SMILES notation. The "smaller than" symbol is used to specify the direction of reading when it's not from left to right. In Figure 5, the SFILE notation "[(iB)] "represents that process-group (iB) is connected as inlet to reactor process-group but not as an outlet. Recycles in the flowsheet are represented by numbers; one for each recycle present. For example, the number 1 in the above example indicates that one outlet of the distillation process-group (dlA/BC)1 is connected to the inlet of the reactor process-group (rxAB/ABCD). Having all the alternatives in the form of SFILES strings will give a computational edge to quickly construct the two-dimensional process flow diagram of a given process alternative and can become a universal way to exchange flowsheet data between process simulation and flowsheet synthesis tools.

### 2.2.2.4 Flowsheet Property Prediction:

In-group contribution based property prediction methods, the property of the molecule is estimated from the contributions of the functional groups. Similiarly property of a process flowsheets represented in the form of process-groups can also be calculated by the contributions of the process-groups present. A flowsheet group contribution based property model can be derived as shown by equation 2.5.

$$f(P) = \sum_{k=1}^{NG} pos_k * a_k \tag{2.5}$$

Where f($P$) is the flowsheet property function, $NG$ is the number of process groups, $a_k$ is the regressed contribution of group $k$, and $pos_k$ is a topology factor

Based on equation 2.5, different flowsheet property models are developed to estimate flowsheet properties, which can be used to screen the generated alternatives. The developed property models are as follows:

*Flowsheet energy consumption index property model:*

The energy consumption property model introduced by d'Anterroches and Gani (2005) predicts the energy consumption of a unit operation (in this case, for various process-groups involving distillation columns), given the corresponding process-groups employed, the driving force (related to the key compounds) and the process-group property contributions.

$$E_x = \sum_{k=1}^{n=NG} Q_k = \sum_{k=1}^{n=NG} \frac{(1+p_k)}{d_{ij}^{k}} * a_k \tag{2.6}$$

Where $E_x$ is the energy consumption of the flowsheet (MkJ/h for Mmoles/h of feed); $Q_k$ is the energy contribution of each process-group; $NG$ is the number of process-groups; $d_{k,ij}$ is the maximum driving force of the process-group $k$ with respect to components $i$ and $j$; $a_k$ is the contribution of the process-group $k$ and; $p_k$ is the topology factor of process-group $k$. The topology factor is defined as

$$p_k = \sum_{i=1}^{nt} \overline{D}_i \tag{2.7}$$

Where, $n_t$ is the number of separation tasks that should be performed before the task $k$ in the ideal case (i.e. separation tasks involving other binary pairs having higher driving force than the selected binary pair) and $D_i$ is the maximum driving force of task $i$. For example, in a separation of a ternary mixture into two products (oA) and (oBC) where the maximum driving force of A/B = 0.12 and B/C = 0.25, $n_t$ = 1 (since only 1 task should have been performed before that is separating the BC mixture) and $D_i$ = 0.25 (the maximum driving force of this task). The contribution factor for different process-groups based on the available driving force can be obtained from Table C1.3 (Appendix C).

*Flowsheet product recovery property model:*

The product recovery property model predicts the percent of the total product recovered in the product streams from the total amount produced in the reaction stage. The total recovery of the product is dependent on the recoveries of the individual separation techniques present in the downstream separation network and the corresponding driving force available for the separation task. For recovery parameters for process-groups refer Appendix C.

$$R_{xa} = \prod_{k=1}^{n=NG} P_{ka} = \prod_{k=1}^{n=NG} SP_{ka} * 100 \tag{2.8}$$

Where, $R_{xa}$ is the recovery of product a; $P_{kx}$ is the recovery contribution of each process-group for product a; $NG$ is the number of process-groups; $SP_{ka}$ is the separation factor of the process-group $k$ with respect to component $a$.

*Carbon footprint property model:*

This model estimates the overall amount of carbon dioxide and other green house gases emissions of the entire process flowsheet as $CO_2$ equivalent. This is estimated based on the energy contribution of each process-group, mass flow rate of the green house gases emitted to the air, and characterization factors of emitted green house gases. The work of Kalakul et al. (2014) is used for characterization factors and the mass flow rates of the green house gases.

$$C_x = \sum_{k=1}^{n=NG} \left( (Q_k) * \sum_{s=1}^{n=NS} (M_s * CF_s) \right) \tag{2.9}$$

Where, $Q_k$ is the energy contribution of each process-group; $NG$ is the number of process-groups; $NS$ is the number of green house gases emitted to air; $M_s$ is the mass flow rate of green house gases emitted to air for 1 Mj/hr of energy spent; $CF_s$ is the characterization factor of the green house gas.

*Flowsheet product purity property model:*

This model estimates the final purity of the selected product. This is estimated based on the purity factor of the final separation task for the selected product. For purity parameters for process-groups refer Appendix C.

$$P_a = PF_{ka} \tag{2.10}$$

Where, $p_a$ is the final purity of product a ; $PF_{ka}$ is the purity factor of separation technique k for component a which is the last purifying step with respect to component a.

### 2.2.2.5 CAMD approach for Process Synthesis:

Having the functional groups, their contributions and their interactions, together with a set of rules to combine the groups into a molecule, allows one to synthesize/design molecules with specific target properties, using a CAMD approach. Similiarly, process flowsheets with specific target properties can also be synthesized by combining the flowsheet building blocks (process-groups) using connectivity rules and evaluating the generated alternatives using flowsheet property models. Figure 6 shows the overview of CAMD based approach for generating flowsheet alternatives.

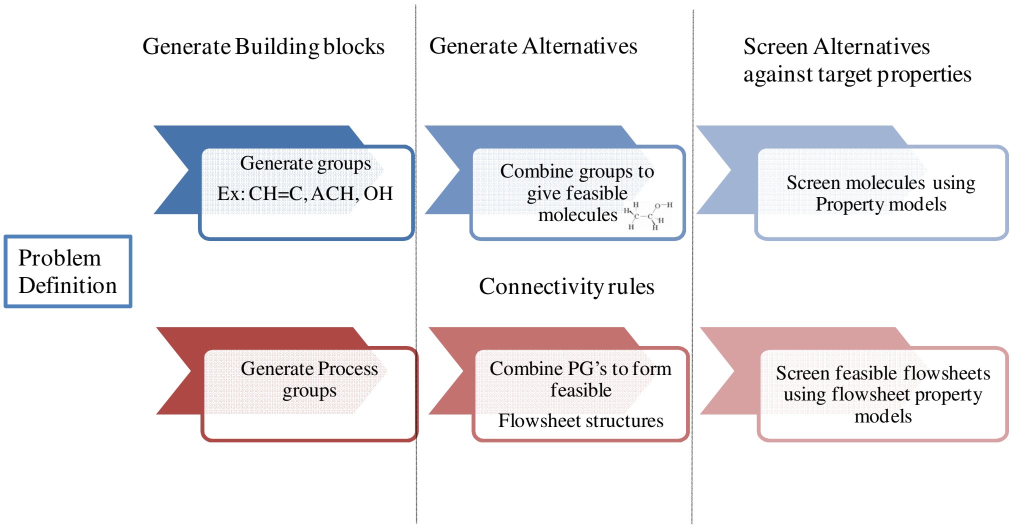


*Figure 6: CAMD based methodology for Process Synthesis*

### 2.2.3 Mass & Energy resolution using simple models:

Amost all the chemical process flowsheets can be represented by combination of simple mass-balance modules of mixers, reactors, component splitters and flow dividers (Seider, Seader, and Lewin 2008). Mixers can be used to represent all kinds of mixing operations, stoichiometric reactors for all types of reactors, component splitters for all separation operations, and dividers for all types of stream-splitting operations. Model equations of the modules are explained in detailed below.

**Mixer:** Mass balance equation across mixer with Nc number of components and Nm number of mixer inlet streams as shown in Figure 7, is given by equation 2.11.

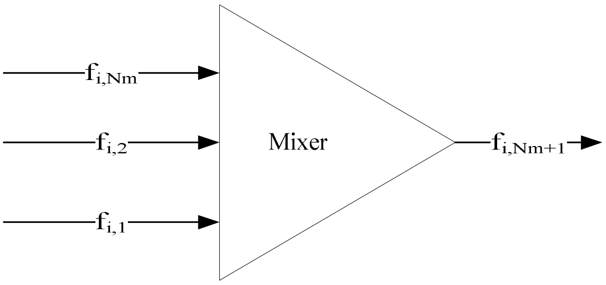


*Figure 7: Control volume and stream connections of mixer*

$$f_{i,Nm+1} = \sum_j f_{ij} \tag{2.11}$$

Where j is the mixer inlet stream counter from 1 to Nm and $f_{ij}$ is the flowrate of component i in stream j.

**Reactor model:** For a single reaction, where k is the limiting reactant and $X_k$ represents the fractional conversion of component k. $V_i$ is the stoichiometric coefficient of component i in the reaction. Stream j enters the reactor as shown in Figure 8. The mass balance equation for the reactor is given by equation 2.12.

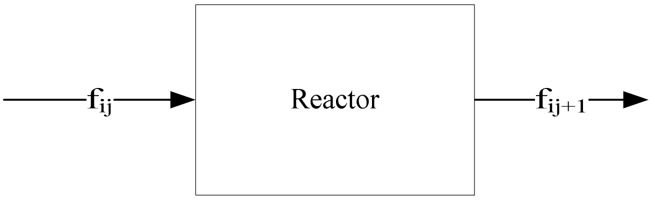


*Figure 8: Control volume and stream connections of reactor*

$$f_{ij+1} = f_{ij} - \frac{V_i}{V_k} X_k f_{kj} \tag{2.12}$$

The energy required for the reator unit operation is calculated using enthalphy balance across the reactor module. Equation 2.13 represents the enthalpy balance across the reactor.

$$Q_r = f_{ij+1} \bullet \Delta h_{j+1} - f_{ij} \bullet \Delta h_j + f_{ij} \bullet \Delta H_r \tag{2.13}$$

Where $Q_r$ is the energy required by the reactor unit operation, $\Delta H_r$ represents the heat of reaction and $\Delta h_j$ represents the enthalpy of the stream j. The enthalpy of a stream is a function of the composition and temperature; the stream composition is obtained from the simple mass balance and the temperature of the streams is calculated based on the process-group definition (refer to appendix C for temperature and pressure settings).

**Splitter model:** This is used in general to represent all the separation unit operations in the flowsheet where the components in the inlet stream are divided between the outlet streams based on the separation factors associated with the separation technique. The model equations for a component splitter with one inlet stream and two product streams as shown in Figure 9 are given by the Equations 2.13 and 2.14.

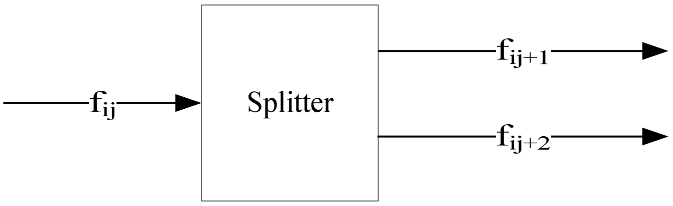


*Figure 9: Control volume and stream connections of splitter*

$$f_{ij+1} = \varepsilon_{is} \bullet f_{ij} \tag{2.14}$$

$$f_{ij+2} = (1 - \varepsilon_{is}) \bullet f_{ij} \tag{2.15}$$

Where $\varepsilon_{is}$ is the separation fraction of component i in stream j+1.

The energy required for the separator unit operation is calculated using enthalphy balance across the module. Equation 2.16 represents the enthalpy balance across the splitter.

$$Q_s = f_{ij+1} \bullet \Delta h_{j+1} + f_{ij+2} \bullet \Delta h_{j+2} - f_{ij} \bullet \Delta h_j \tag{2.16}$$

Where $Q_s$ is the energy required by the splitter unit operation and $\Delta h_j$ represents the enthalpy of the stream j. Again, the enthalpy of a stream is function of composition and temperature; the stream composition is obtained from the simple mass balance while the temperature of the streams is estimated based on the process-group definition (refer appendix C for temperature and pressure settings).

**Divider model:** This model is used to represent unit operations where the outlet streams have the same composition like purge and recycle streams. The model equations for a divider with one inlet stream and two product streams, as shown in Figure 10, are given by Equations 2.17 and 2.18.

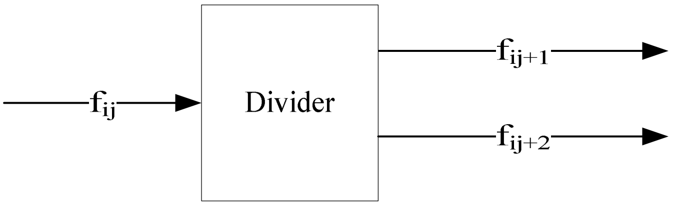


*Figure 10: Control volume and stream connections of splitter*

$$f_{ij+1} = \beta_D \bullet f_{ij} \tag{2.17}$$

$$f_{ij+2} = (1 - \beta_D) \bullet f_{ij} \tag{2.18}$$

Where $\beta_D$ is the split fraction of component i in stream j+1.
The energy balance equation of the divider is similar to splitter as shown in Equation 2.16 since divider module can be considered as a special case of splitter.

### 2.2.4 Driving Force (DF):

The driving force concept was introduced by Bek-Pedersen and Gani (2004) for synthesis and design of distillation separation processes. The driving force for any process is defined as the difference in compositions of a specific compound i in two co-existing phases. So, for a distillation process, it is the difference in the liquid ($x_i$) and vapor ($y_i$) compositions for component i. Mathematically it is written as shown in equation 2.19.

$$DF_{ij} = y_i - x_i \tag{2.19}$$

As shown in the Figure 11, the driving force is a concave function with respect to composition with a well-defined maximum. Since energy needs to be added to or removed from the system in order to create and maintain two co existing vapor-liquid phases, the value of the DF can be related to energy added or removed. If the DF is large, less energy is required, while if the DF is small, more energy is required to separate the mixture. By targeting the separation task with highest driving force first, Bek-Pedersen and Gani (2004) proved that near optimal separation sequence can be generated without performing any rigorous mass or energy balance calculations.

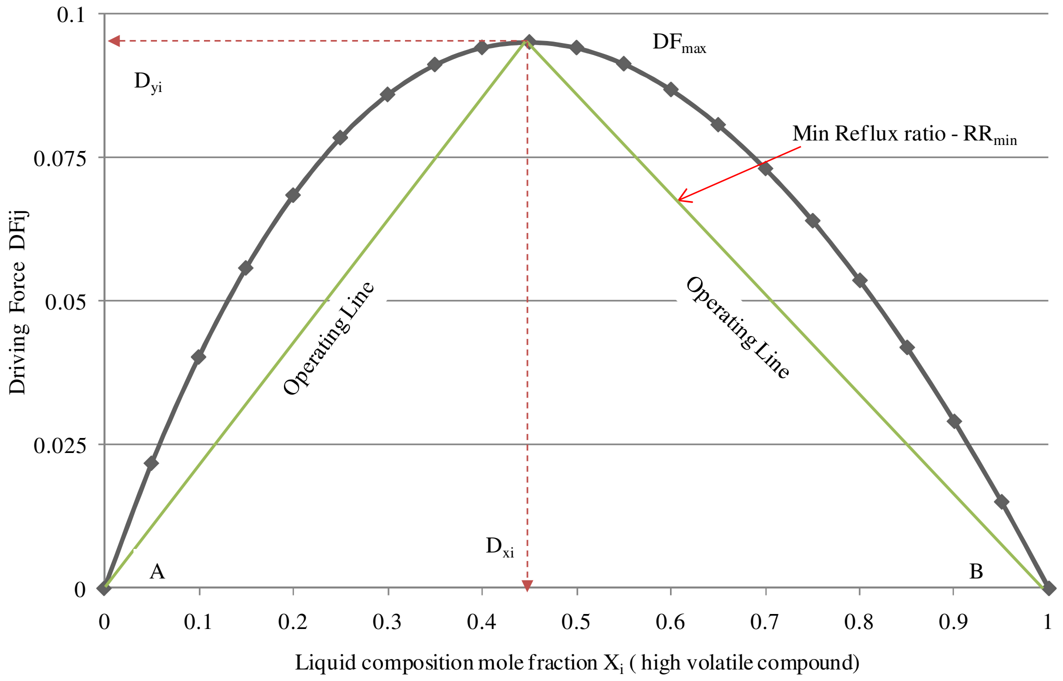


*Figure 11: Driving force diagram*

The driving force approach provides the basis for the determination of distillation design variables like number of stages, feed stage location, reflux ratio etc. In Figure 11, the lines $AD_{yi}$ and $BD_{yi}$ represent operating lines corresponding to minimum reflux ratio. Any other operating lines from the product specifications A, B will have reflux ratios greater than the identified minimum. Therefore, distillation design targeting the highest driving force will always have the lowest reflux ratio, which also corresponds to near optimal design in terms of energy consumption.

### 2.2.5 Reverse Simulation Approach:

The reverse simulation approach is a method to calculate the design parameters of the unit operations from the process variables. The term "reverse" is used to highlight the difference between the conventional process simulations where process variables are calculated for assumed values of design parameters.

For example, the driving force concept, explained in section 2.2.4, can be used to calculate the design parameters of a distillation separation process. The synthesis and design method for distillation sequences is then based on the maximum driving force available and its location. This can then be used to estimate the column design parameters, like number of stages, feed location and reflux ratios etc.

Consider a distillation process-group (dlA/B) to separate a methanol-water mixture. The feed compositions and compound data are given in Table 9. The minimum purity of the distillate required is 99.5 mol%. The key components A and B are methanol and water respectively. From the driving force diagram (Figure 12) between methanol and water at 1 atm, the maximum driving force is $F_{di,\ max}$= 0.38 at $D_x$=0.25. From Table A1.1 (Appendix A) the precalculated values for number of ideal stages $N_{ideal}$=13 and minimum reflux ratio $RR_{min}$= 0.82 for a distillate purity of 99.5%. Finally, the feed location for this column is calculated from $N_{ideal}$ and $D_{x,}$ using $Nf = N_{ideal} (1- D_x)$, resulting in a feed location at stage 10.

*Table 9: Feed properties for the process-group (dlA/B)*

| **Compound** | **Value** | **Units** |
|---|---|---|
| Methanol (A) | 310.04 | kgmol/hr |
| Water (B) | 1037.96 | kgmol/hr |
| Temperature | 353.6 | K |
| Pressure | 1 | atm |

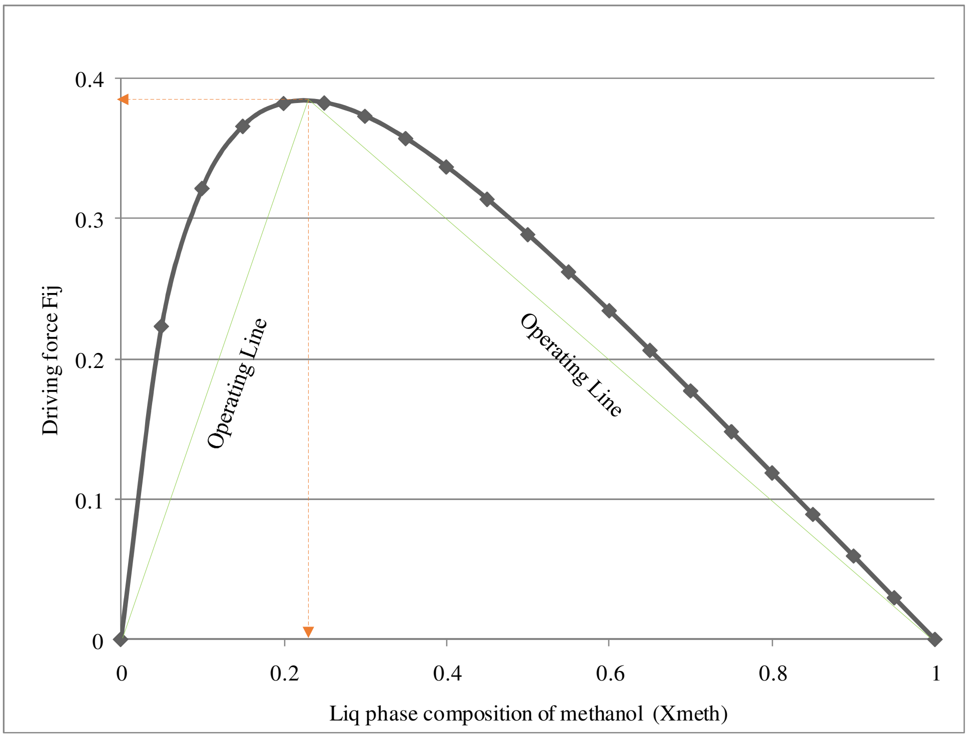


*Figure 12: Driving force diagram for key pair Methanol/Water*

Similarly, using attainable region (AR) concept, the kinetic based reactor process-group can be designed using reverse simulation approach. The AR concept provides a graphical method for the synthesis of chemical reactor networks (Horn.F 1964; Hildebrandt and Glasser 1990; Glasser and Hildebrandt 1997). Once the AR diagram has been constructed for a given reaction mechanism, the idea is to use the location of the maximum value of the objective function, which can be product concentration, ratios etc., as the basis for reactor design. From the generated AR diagram, other important process variables, such as residence time, temperature, and reactor volume, can also be calculated.

The following information is obtained from the selected kinetic process-group to complete the AR analysis:

- Nature of components in the reactions
- Complete reaction mechanism and associated kinetics

Attainable region (AR) analysis comprises of six major steps:

1. **Selection of fundamental processes:** In this step, all the physical and chemical phenomena present in synthesis of a reaction system like reaction, mixing, heat transfer and mass transfer are considered.
2. **Selection of state variables:** The state of the system is characterized by state variables. State variables that describe the fundamental processes like concentrations, mass fractions, reaction conversions, etc. are chosen.
3. **Define the fundamental process vectors:** In this step, the fundamental process vectors are defined, such that they represent the instantaneous change in the characteristic vector or state, if that fundamental process occurs on its own. For instance, the reaction vector, R(C) defined at C represents the instantaneous change in C if only reaction occurs.
4. **Constructing AR:** In this step, the attainable region graph is constructed in accordance to the necessary conditions given by Hildebrandt and Glasser (1990). According to Hildebrandt and Glasser, it is necessary that the attainable region **A** is such that:
    a. It is convex.
    b. No reaction vector on the boundary of **A** points outwards.
    c. No reaction vector in the complement of **A** can be extrapolated backwards into **A**.
    d. No two points on a PFR in the complement of **A** can be extrapolated back into **A**.

    A brief description on the steps involved in construction of the AR:

    - Draw the PFR(s) from the feed point(s).
    - Allow mixing between all the points that can be achieved by the PFR(s). This process is known as finding the convex hull of the curve(s).
    - Check whether any reaction vectors point out of the surface of the convex hull. If the reaction vector points outwards over certain regions, then find the CSTR(s) with feed points in the convex hull that extend the AR the most. If no reaction vectors point outwards, then check whether necessary conditions (c) and (d) are meet. If they are not met, extend the region using the appropriate reactor.
    - Repeat the last two steps, alternating between PFR's and CSTR's until no reaction vectors point out over the region, and necessary conditions (c) and (d) are met.
5. **Boundary interpretation:** From the generated AR, it is possible to determine the process layout to achieve a specific output. For a particular output of interest there will be path from the input to the output point. This path can be interpreted in terms of the sequence of fundamental processes required to follow the path. There is usually only one path to a particular point on the boundary and an infinite number of paths to any point in the interior of the attainable region.
6. **Optimization of objective function:** Since the optimum value for the objective function has already been interpreted as a process specification and boundary, the result is that attainable region analysis determines not only the best value for the objective function, but also the best process design (the best process layout or sequence and the best

operating conditions). It is also possible to establish the sensitivity of the objective function to various changes to the process design.

**Example of reverse simulation for the kinetic based reactor process group:** In this example, the attainable region analysis is carried out to find the best design for reactor process group (rA/ABCDE). The following constant density, isothermal reaction mechanism is used as example (Denbiqh 1958).

$$A \xrightarrow{k1} B \xrightarrow{k2} C \tag{2.20}$$

$$A \xrightarrow{k3} D \tag{2.21}$$

$$B \xrightarrow{k4} E \tag{2.22}$$

The initial characteristics of the reaction network are shown in Table 10. The problem consists of finding the best reactor network that maximizes the amount of product B for a feed of pure A.

In this example, as a fundamental process is mixing, perfectly mixed reaction (CSTR) and reaction with no mixing (PFR) are considered. The mass balance equations for a PFR are:

$$\frac{dCa}{dt} = -Ca \bullet \left(k_3 + k_1 \bullet Ca\right) \tag{2.23}$$

$$\frac{dCb}{dt} = k_1 \bullet Ca \bullet Ca - Cb \bullet \left(k_4 \bullet Cb + k_2\right) \tag{2.24}$$

$$\frac{dCd}{dt} = k_3 \bullet Ca \tag{2.25}$$

$$\frac{dCe}{dt} = k_4 \bullet Cb \bullet Cb \tag{2.26}$$

$$\frac{dCc}{dt} = k_2 \bullet Cb \tag{2.27}$$

*Table 10: Rate constants and initial concentrations for selected reaction network.*

| **Rate constant** | **Value** | **Units** |
|---|---|---|
| $k_1$ | 6 | Lit/mol*sec$^1$ |
| $k_2$ | 0.6 | 1/sec$^1$ |
| $k_3$ | 0.6 | 1/sec$^1$ |
| $k_4$ | 0.6 | Lit/mol*sec$^1$ |
| **Initial concentrations** | | |
| $Ca_0$ | 6 | mol/Lit |
| $Cb_0$, $Cc_0$, $Cd_0$ , $Ce_0$ | 0 | mol/Lit |

The mass balance equations for a CSTR are:

$$Ca - Ca_0 = \tau(-Ca \bullet \left(k_3 + k_1 \bullet Ca\right)) \tag{2.28}$$

$$Cb - Cb_0 = \tau(\ k_1 \bullet Ca \bullet Ca - Cb \bullet (k_4 \bullet Cb + k_2)) \tag{2.29}$$

$$Cd - Cd_0 = \tau(k_3 \bullet Ca) \tag{2.30}$$

$$Ce - Ce_0 = \tau(k_4 \bullet Cb \bullet Cb) \tag{2.31}$$

$$Cc - Cc_0 = \tau(k_2 \bullet Cb) \tag{2.32}$$

According to the problem specification, we wish to maximize B so the concentration term Cb is a state variable and Ca is also a state variable, as Ca is the independent variable which is present on the right hand side of all the equations (2.23 – 2.32).

**Construction of Attainiable region:**

1. Draw the PFR from the feed point. From equations 2.23 and 2.24, we obtain

$$\frac{dCb}{dCa} = \frac{k_1 \bullet Ca \bullet Ca - Cb \bullet (k_4 \bullet Cb + k_2)}{-Ca \bullet (k_3 + k_1 \bullet Ca)} \tag{2.33}$$

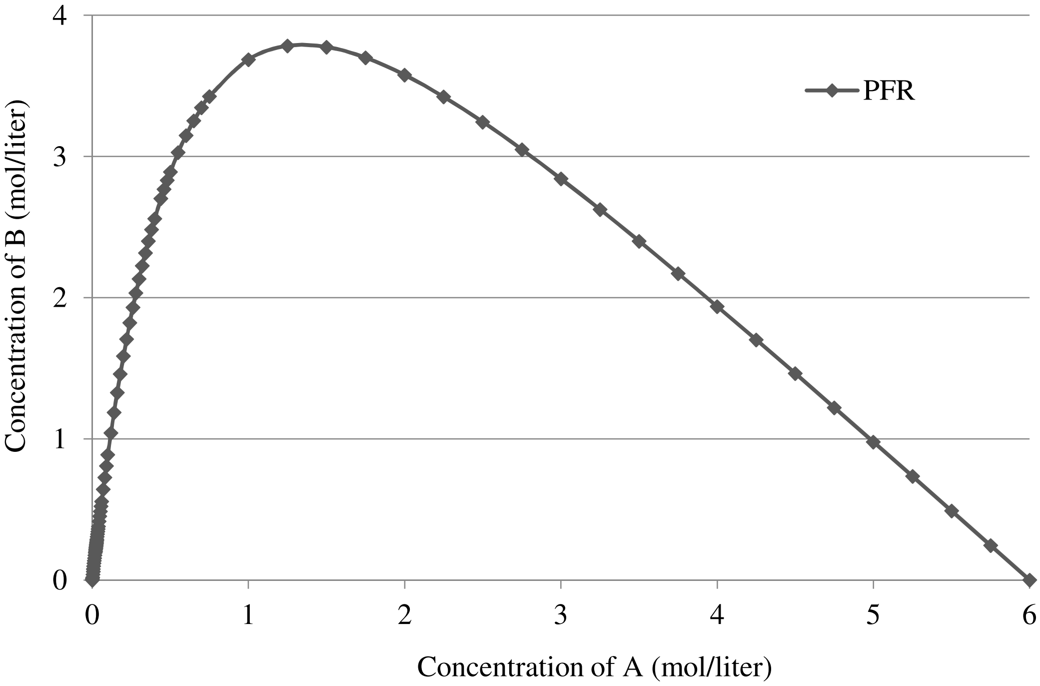


*Figure 13: State-space diagram for PFR*

2. Find the convex hull of the curve: From the Figure 13, it is clear that the trajectories are convex and the rate vector computed along the boundary is tangent, it can be concluded that the trajectory bounds the attainable region.
3. Draw the CSTR from the feed point: It can be seen from the Figure 14, that when PFR and CSTR trajectories start from the same feed point, there is a large overlap in the behavior of the two reactors.

4. Finding the convex hull of the CSTR curve: Since from the Figure 14, it is clear that the trajectories are convex.

**Boundary Interpretation:** In this example, since single PFR provides the maximum production B with respect to pure feed stream of A, the state space diagram of the PFR defines the attainable region.

**Optimum value of the objective function:** In this example, the objective function is to maximize production of B. So from the AR plot, the maximum concentration of B (3.8 mol/liter) is attained in a single PFRs.

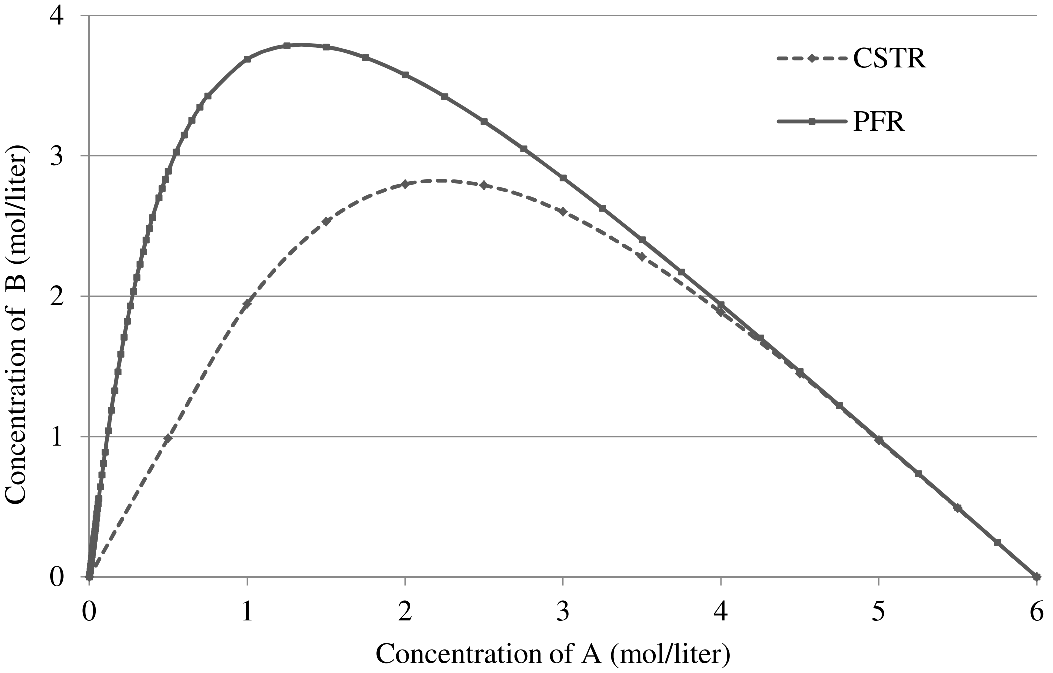


*Figure 14: Addition of CSTR (step 3)*

### 2.2.6 LP Transshipment Model:

Transshipment means transportation or shipment of commodities or goods from one destination to another. Transshipment models are variations of the well know transportation problem, which are primarily used in operation research to generate optimal network for transporting goods. Papoulias and Grossmann (1983) have formulated the heat integration problem of a process as linear programming (LP) Transshipment model to minimize the total utility cost for a given set of hot and cold streams.

In this model Papoulias and Grossmann treat all the hot streams as source nodes and cold streams as destination nodes. Heat can then be regarded as a commodity that must be transferred from the sources to the destinations through some intermediate stages. In a given temperature interval, if all the heat available is not allocated to destinations (cold streams), then the excess is cascaded to the lower temperature intervals through residuals ($R_k$ , $R_{k-1}$).

The Transshipment model to minimize the total utility cost for a given set of hot and cold streams can be formulated as follows:

First, based on the given hot and cold streams the entire temperature range is partitioned into *k* temperature intervals having a temperature change of $\Delta T_k$. For all temperature intervals identified, the following index sets are defined.

$H_k = \{ i \mid \text{hot stream } i \text{ supplies heat to interval } k \}$

$C_k = \{ j \mid \text{cold stream } j \text{ demands heat from interval } k \}$

$S_k = \{ m \mid \text{hot utility } m \text{ supplies heat to interval } k \}$

$W_k = \{ n \mid \text{cold utility } n \text{ extracts heat from interval } k \}$

$S =$ set of hot utilities

$W =$ set of cold utilities

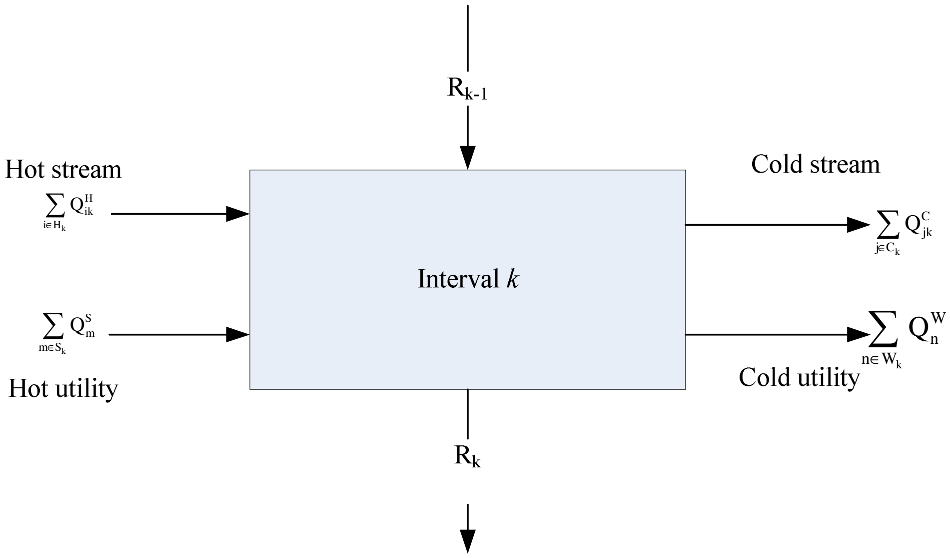


*Figure 15: Heat flows in interval k*

For a defined temperature interval k, as shown in Figure 15, we will have the following known parameters and variables.

Known parameters:

- $Q^H_{ik}, Q^C_{jk}$ Heat contents of hot streams *i* and cold stream *j* in the temperature interval k. which are given by the following equations:

$$Q^{H}_{ik} = F_i (c_p)_{ik} \Delta T^{i}_{k} \tag{2.34}$$

Where $F_i$ is the flowrate of hot stream $i$ , $C_p$ is the heat capacity and $\Delta T^{i}_{k}$ is the temperature of hot stream *i* entering the temperature interval *k*.

$$Q^{C}_{jk} = F_j (c_p)_{jk} \Delta T^{j}_{k} \tag{2.35}$$

Where $F_j$ is the flowrate of cold stream $j$ , $C_p$ is the heat capacity and $\Delta T^{j}_{k}$ is the temperature of cold stream *j* entering the temperature interval *k*.

- $C_m, C_n$ unit costs of hot utility *m* and cold utility *n*

Variables:

- $Q^{S}_{m}, Q^{W}_{n}$ Heat loads of hot utility *m* and cold utility *n*.
- $R_k$ Heat residual exiting temperature interval *k*.

The minimum utility cost for a given set of hot and cold processing streams can then be formulated as the following LP:

$$\min Z = \sum_{m \in S} c_m Q^{S}_{m} + \sum_{n \in W} c_n Q^{W}_{n} \tag{2.36}$$

*s.t.*

$$R_k - R_{k-1} - \sum_{m \in S_k} Q^{S}_{m} + \sum_{n \in W_k} Q^{W}_{n} = \sum_{i \in H_k} Q^{S}_{ik} - \sum_{j \in C_k} Q^{C}_{jk} \tag{2.37}$$

The constraint (equation 2.37) represents simple heat balance for each temperature interval defined for the integration problem. In the objective function (equation 2.36), if the cost coefficients $C_{m,}$ $C_n$ are set to unity, the above formulation will yield solution for minimum utility consumption. The temperature interval k where the residual heat flow $R_k$ is zero corresponds to a pinch point.

### 2.2.7 Design & Analysis of Hybrid Separations:

Distillation is one of the most used separation techniques in chemical process industry. As a separation technique, it is one of the most energy intensive, and with regards to efficiency, it is amongst the processes having the least thermal efficiency (Pellegrino et al. 2004). Even though distillation is ranked among the processes with the least thermal efficiency, nearly 80 % of all vapor-liquid separations in chemical process industries are performed by distillation (Wankat 2011). According to the US Department of Energy, separation technologies from all the manufacturing industries used nearly 150 million kW of energy in 2005 (Angelini et al. 2005), out of which, distillation (49 %), drying (20%) and evaporation (11%) accounted for more than 90 % of the total energy consumption. Operational costs of distillation columns are proportional to the energy requirements in the reboiler, which vaporizes a part of the liquid product coming out of the bottom stage of the column. This vapor stream travels up through the column during which, the more volatile compounds in the stream are enriched by stripping it from the liquid flowing down. So the amount of vapor generated, or the reboiler duty, is directly proportional to the required enrichment or distillate product purity. Tula et al. (2016) established a relationship between reboiler duty and distillate purity by carrying out a simulation based analysis of different binary mixtures of varying degree of separability (measured in terms of relative volatility).

The results of the simulations are presented in Figure 16 for various binary mixtures characterized by their maximum driving force and chemical type. These Figures are generated for different classes of binary mixtures characterized by their maximum driving force. For any new binary mixture, after calculating their maximum driving force, these curves can be used to identify the purity versus reboiler duty for distillation columns selected to separate the mixture. The curves are independent of the species in the sense that for a similar maximum driving force the relative reboiler duty required as a function of purity of the distillate product is similar, irrespective of the binary mixture.

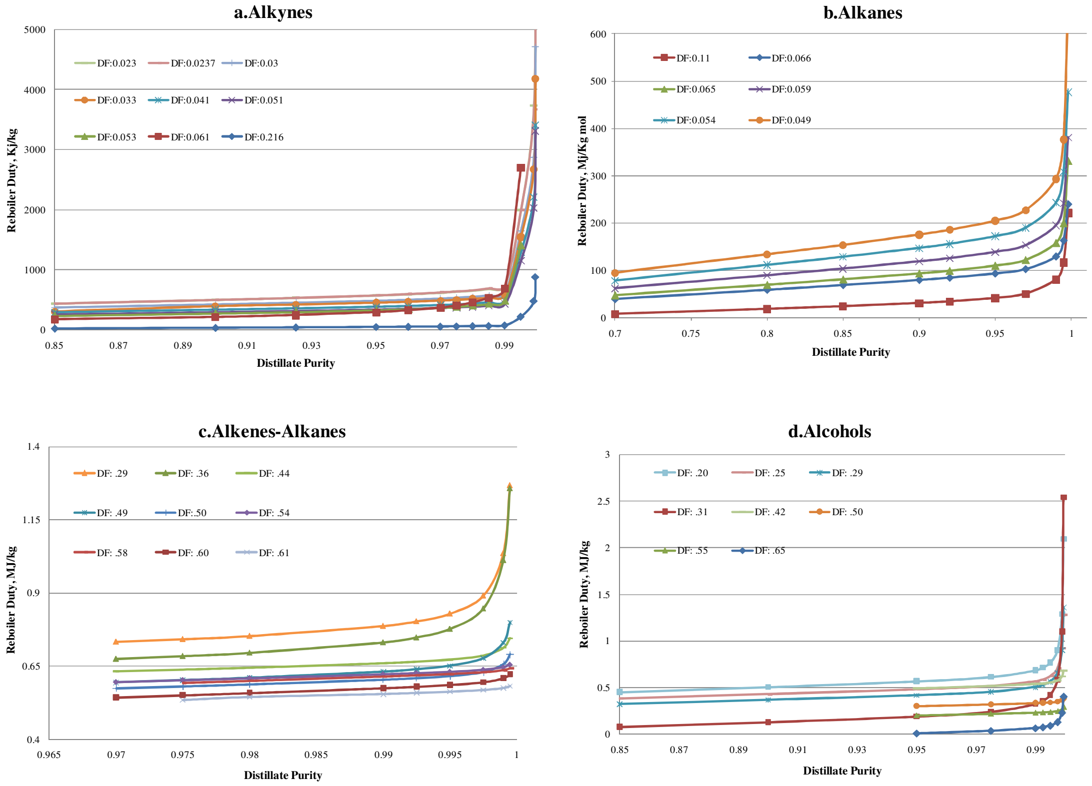


*Figure 16: Reboiler duty versus distillate product purity for different compound classes.*

From Figure 16, the following points can be observed:

1) The amount of energy required by the reboiler increases steadily (proportionally) until a certain distillate purity. Beyond this point, the reboiler duty increases exponentially with distillate purity. For example, in Figure 16 for Alkanes, the energy required by most of the systems increases steadily until the product purity reaches 95 %; for higher purity the energy required per kg mol of feed increases exponentially. That is, more than 50% of the total energy is required, for example, to increase the product purity from 95% to 99%. Figure

16 indicates a general trend with respect to distillate product purity (specification) versus duty. Note, however, that the change in the slope of the curves is a function of the maximum driving force of the mixture. Figure 16 also shows that as maximum driving force for the mixture to be separated decreases, more energy is required to achieve the same distillate product purity.

2) Since the energy required for distillation depends on the driving force of the system, it is possible to estimate the energy savings (using Figure 16) in distillation by selecting one of the reboiler duties versus product purity curve and then selecting a cut-off value for the single distillation operation. In Figure 17, the corresponding carbon footprints in the plots of energy required versus distillate product purity are also shown. The carbon footprint is calculated as a function of energy consumed through a model reported by Kalakul et al. (2014). It estimates the overall amount of carbon dioxide and other greenhouse gases emitted as $CO_2$ equivalent.

$$CO_{2_{eq}} = M^{PRO}_{GHG,Air} * CF^{GWP}_{GHG,Air} \tag{2.38}$$

Where, $CO_{2eq}$ represents the carbon footprint in terms of $CO_2$ equivalent, $M_{GHG,\ Air}$ is the mass flow rate of greenhouse gases emitted to air for 1 MJ/hr of energy spent and $CF_{GHG,Air}$ is the characterization factor of the greenhouse gas emitted to air.

The energy to be saved from the distillation operation is given by

$$Q_{savings} = \left(\frac{Q_{target} - Q_{intermediate}}{Q_{target}}\right) * 100 \tag{2.39}$$

Where, $Q_{target}$ represents the energy required to distillate the product to 99.5 % purity, $Q_{intermediate}$ is the energy required to distill the product to 90% purity and the $Q_{savings}$ is the energy savings associated with hybrid distillation sequence.

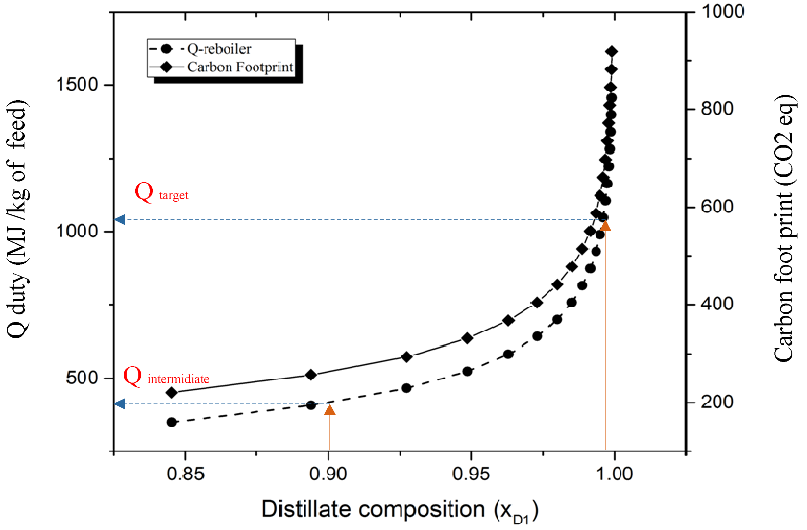


*Figure 17: Reboiler duty and carbon footprint as a function of distillate product purity*

Based on the analysis, it is clear that 30-50 % of energy used in distillation columns can be avoided by replacing the less efficient region of the distillation separation task with a more efficient separation technique. One potential separation technique, which can be considered for the hybrid scheme, is the use of membrane based separation techniques like pervaporation, vapor/liquid permeation membranes. A membrane is a separation technique that has preferential affinity towards one or more of the compounds in the mixture to be separated. Since membrane separation techniques do not require any heating, unlike conventional thermal separation processes, they could be good candidates for hybrid schemes if the appropriate membranes having the required permeability's could be found. However, the major limitation associated with using membrane-based separations is their inability to handle high volumes of the feed mixture to be separated and the associated capital investment (not to mention operability problems such as fouling). The membrane area required in any membrane based separation technique, is dictated by flowrate of the permeating compound and the membranes permeability. This makes using membrane-only solutions very capital intensive and not practical for continuous processes with high flowrates.

$$A_m \propto \dot{m} \tag{2.40}$$

$$A_m \propto 1 / P_i \tag{2.41}$$

Where $A_m$ the membrane area, $\dot{m}$ and $P_i$ represent the permeate flow rate and permeability of compound i, respectively.

Therefore, unlike distillation columns, the limiting factor in case of membranes is the flux and the membrane area needed to perform the desired separation.

**Pervaporation Process:**

This process is based on dense non-porous membranes that are typically made of ceramic, zeolite or polymeric materials. When a binary/multi-component liquid mixture is brought in contact with the active feed side of the membrane, the permeable compound of the mixture first diffuses through the membrane and then this permeated compound evaporates due to the prevailing low pressure on the permeate side, which is later recovered by vacuum. Figure 18 shows a schematic of a typical membrane process using a condenser to generate the permeate vacuum. The driving force for this process is the difference in the partial pressures of the mixture across the membrane along with differences in permeability of individual compounds through the membrane module (Aptel et al. 1972; Rautenbach, Herion, and Meyer-Blumenroth 1991). Since pervaporation is almost independent of vapor liquid equilibrium, this separation technique can also be used to separate difficult mixtures involving azeotropes & close boiling systems.

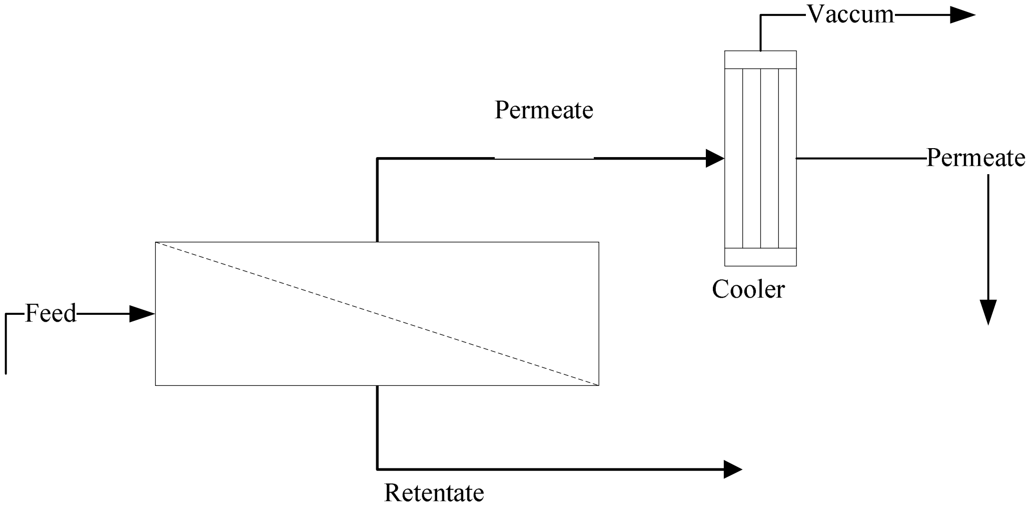


*Figure 18: Typical membrane separation scheme*

Currently pervaporation technique is widely used in dehydration of organic solvents, like ethanol, isopropanol, etc., which are otherwise difficult to separate using traditional thermal based separation techniques.

**Vapor Permeation Process:**

This separation technique is similar to pervaporation except that the feed is in the vapor phase and there is no change of phase during the separation process. The gas feed, at elevated pressure, is brought in contact with the membrane, which selectively permeates one of the components of the feed mixture. The main advantage of this process when compared to pervaporation is that since no phase change is involved, the corresponding energy needed for heat of vaporization in pervaporation is avoided and also there is usually no temperature drop across the membrane (Böddeker 1990; Ito, Feng, and Sasaki 1997). Currently this technique is widely used in separation of hydrogen from nitrogen (Baker 2004), carbon monoxide from argon, and gas dehumidifying (Cen, Y., Lichtenthaler 1995).

**Distillation-membrane based hybrid separation process:**

In order to achieve any separation, the driving force of the system must be greater than zero. Consider the separation of methanol and water. Figure 19 shows the driving force for the separation task using distillation and membrane unit operations, respectively. However, on close observation of Figure 19, it is clear that both distillation and membrane separation tasks have their regions of efficient operations, which are functions of the desired separation (product purity or flux). For distillation, the needed reboiler duty versus product purity curve is also shown. So replacing the part of the separation where distillation has very low driving force (or requiring most of the energy) with a membrane module that has higher separation efficiency in this region will make sure that both the separation techniques are operated at their high efficient regions (Tula et al. 2016). Thereby, a potentially very promising energy saving (compared to the use of only distillation) or low capital cost (compared to the use of only membrane based separation) hybrid scheme is developed (see Figure 20, where the flowsheet for the hybrid distillation-membrane module is shown).

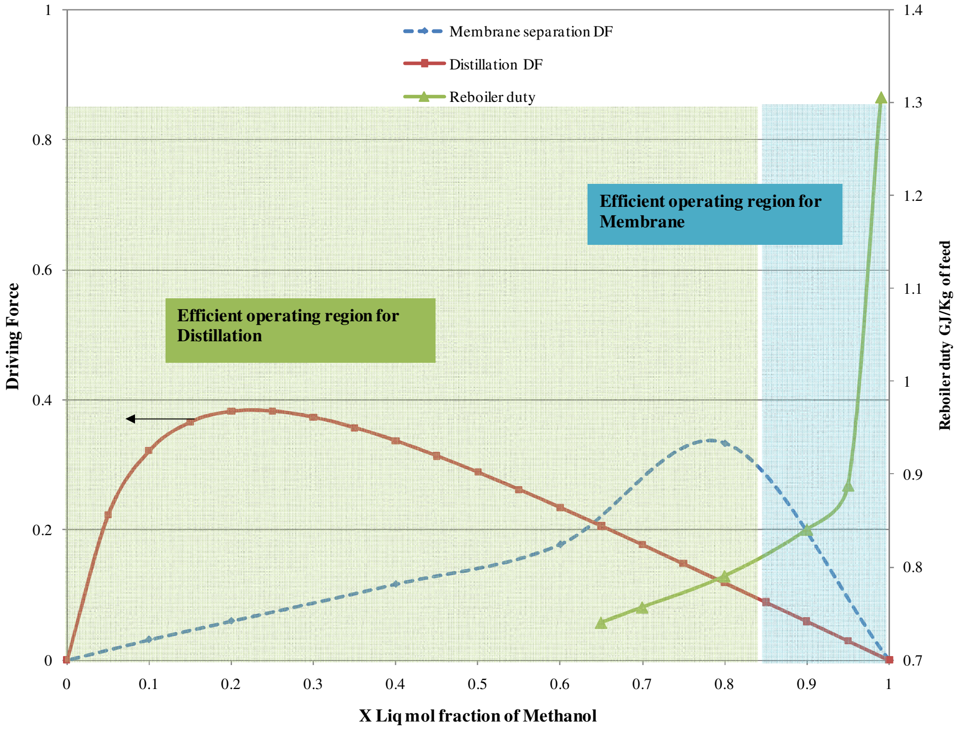


*Figure 19: Driving force for Methanol – Water systems (Distillation and Membrane separation).*

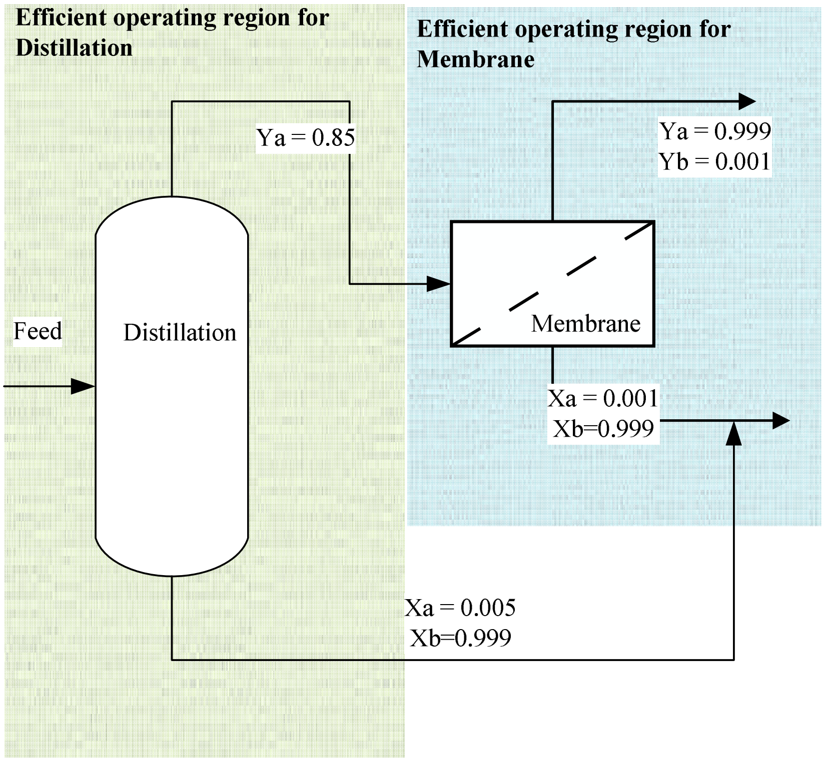


*Figure 20: Hybrid separation scheme.*

# 3

# COMPUTER-AIDED METHOD FOR SUSTAINABLE PROCESS SYNTHESIS-DESIGN AND ANALYSIS

In this chapter, the proposed method for sustainable process synthesis-design is presented along with work and data flow. Each stage in the decomposition-based method is explained in detail along with the corresponding algorithms developed for each step.

## 3.1 OVERVIEW OF SUSTAINABLE PROCESS SYNTHESIS-DESIGN AND ANALYSIS METHOD

The proposed method for sustainable process synthesis-design and analysis has eight steps. Its workflow together with the supporting methods and tools for each step are outlined in Figure 21. Step 1 is the problem definition step where synthesis problem is defined along with specifications and constraints to be satisfied by the final design. In Step 2, the synthesis problem is analyzed and necessary information is obtained to solve the synthesis problem. In step 3, based on the generated information, process-groups feasible for the defined problem are selected and initialized. In step 4, process alternatives are generated using the selected process-groups. In step 5, ranking of the generated process alternatives is carried out based on the target specifications defined in step 1. In step 6, the design parameters are calculated for the top ranked alternatives. In step 7, the selected designs are verified using rigorous models and process analysis is carried to identify the process bottlenecks. In step 8, the identified process bottlenecks are targeted using innovative design strategies to further improve the process. In the following sections, each one of the eight stages of the method is described in detail.

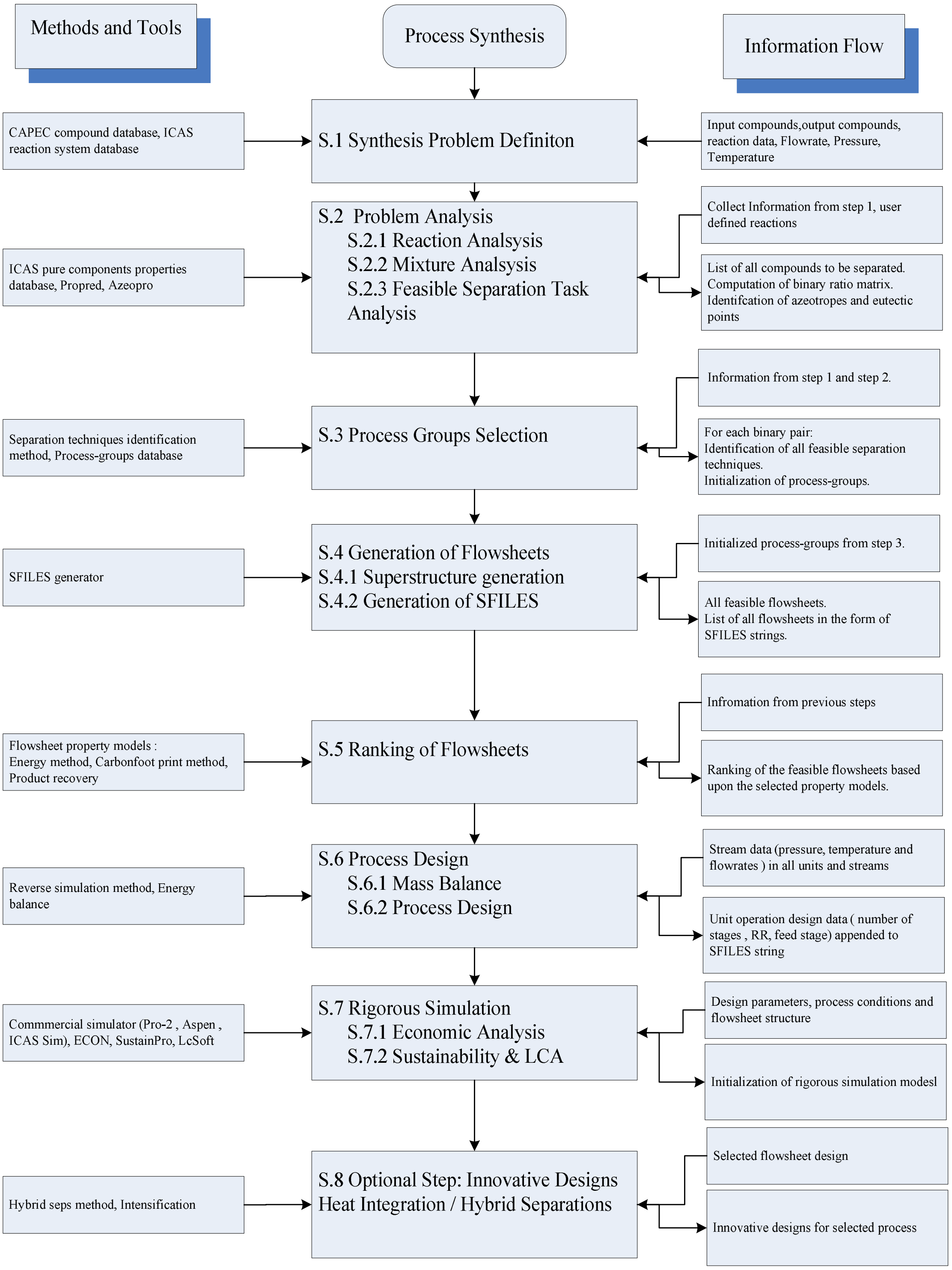


*Figure 21: Sustainable Process Synthesis-Design and Analysis Method*

### 3.1.1 Synthesis Problem Definition

The objective of this step is to define the synthesis problem, design constraints and the performance criteria to generate the optimized solution. The detailed information flow of this step is illustrated in Figure 22.

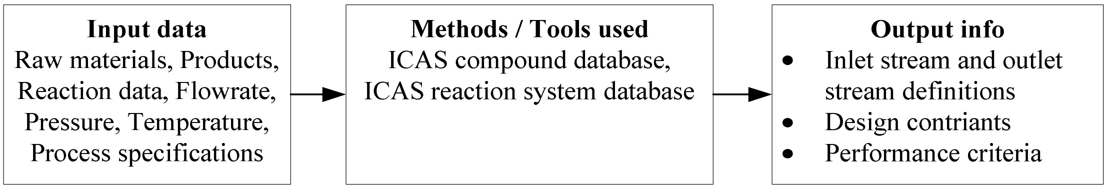


*Figure 22: Method/Tools and information flow for step 1 of the method*

This step is split in two tasks:

1) Task 1: The user provides the structural definition of the synthesis problem by defining the raw materials (input streams) and desired products (outputs stream) of the process. This structural definition also includes the individual component flow rates, temperature and pressure of all the streams.
2) Task 2: In this task, the process specifications (example product purity, product recovery etc.) and the performance criteria based on which the generated alternatives are screened is defined.

As only input and output materials are known for a new process synthesis problem, only the terminal process groups, representing the inlet and outlet streams of the desired process, are known in the flowsheet structure that needs to be determined. Then the remaining task is to determine the correct sequence of unit process operations represented by process-groups that will produce the desired product matching the flowsheet performance targets. In addition, for retrofit problems where one seeks to improve upon an existing process flowsheet, task one includes the definition of already interconnected unit operations together with the available raw materials inlets and desired product outlets.

### 3.1.2 Synthesis Problem Analysis

This step is one of the most important of the total method as the objective of this step is to generate the information required for solving the synthesis problem. Analysis of the process synthesis problem is performed to further define the problem by knowledge bases and physical insight methods. All the supporting tools and methods along with the information flow in this step are shown in Figure 23.

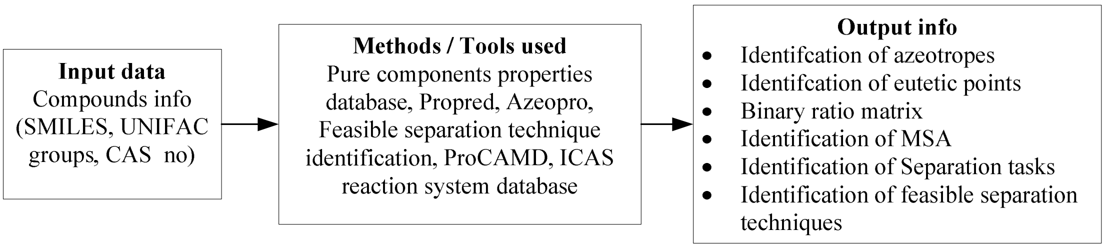


*Figure 23: Method/Tools and information flow for step 2 of the method*

The outcomes of the analysis include:

i. List of all chemical species in the synthesis problem, including reaction intermediates and/or any mass transfer agents.
ii. Reactions, if needed, to convert the given raw materials to desired products.
iii. List of all the possible separation tasks along with feasible separation techniques.

This analysis is carried out through the following three tasks: (i) reaction analysis, (ii) mixture analysis and (iii) feasible separation task identification.

1) **Reaction Analysis:** In the analysis task, the list of chemical species that should be formed by the reactions are identified by comparing the chemical species available as raw materials and products. Then, for each chemical species identified, a database search is performed to find the reaction mechanisms yielding the identified compound. This approach is iterative, as possible reactions may imply the need to provide reactants that are not currently specified. All new reactants or by-products from the matched reaction mechanisms are added to the synthesis problem.

2) **Mixture Analysis:** In the analysis task, pure component and mixture property analysis is performed for all the chemical species listed in the problem to generate information/data that can be used for identification of separation task and feasible separation techniques to achieve the separation task.

   Pure component analysis: The pure component analysis is performed by retrieving a list of 22 pure component properties (see Table 11) from the ICAS database (R Gani et al. 1997; R Gani 2002). For compounds missing data or for new compounds, the properties are calculated using ProPred (property prediction tool box) which is part of the Integrated Computer Aided System (ICAS) (R Gani et al. 1997; R Gani 2002). ProPred uses $GC^+$ based property models for estimation of thermo-physical, transport related and environmental related properties along with their uncertainties.

   Mixture property analysis: This analysis is performed in terms of the binary pairs of all the chemical species identified in the synthesis problem. For each binary component pair identified, analysis is performed to identify possible azeotropes, eutectic points or potential mass separation agents. Azeopro (Azeotrope analysis toolbox from ICAS), which is based on a hybrid approach of database search and calculations, is used to identify azeotropes present in the system and to provide potential solutions to separate them. The solutions to separate the azeotropes range from simple pressure swing distillation to using external mass transfer agents. The potential MSA (mass separating agents) are found by solubility analysis from the pure component property and from a list of commonly used solvents. If the solvent is not found for an identified azeotrope from the known solvents database, then ProCAMD (computer-aided molecular design toolbox), which is part of ICAS, is used to design a suitable solvent based on the properties of the separation technique. ProCAMD employs the group contribution based molecular design concept to generate feasible chemical structures and tests them to check for their match of the desired target properties.

3) **Feasible Separation Task Identification:** In this task feasible process operation techniques are identified using the Jaksland et al. (1995) physical insights-based method as explained in section 2.2.1. Jaksland's method is based on the principle that every process operation task can be associated to one or more pure component properties. According to the method, for a separation between two components and a given operation task, it is possible to assess if the operation task is feasible by comparing the ratio of the corresponding pure component properties. If the property ratio is greater than the threshold value corresponding to the feasibility of the separation task along with any additional property constraints required to be satisfied, the separation technique is considered as feasible. For example, a conventional distillation separation task (one feed and two products) is feasible if the following conditions are satisfied: the ratio of boiling points is greater than 1.02 and no azeotropes exist. So based on the pure component analysis and mixture property analysis, a table of property ratios for all the binary pairs is generated and is used to identify the feasible separation tasks.

*Table 11: 22 pure component properties used in Mixture analysis task*

| Symbol | Pure Component Property |
|---|---|
| $M_w$ | Molecular Weight (g/mol) |
| $\omega$ | Acentric Factor |
| $T_c$ | Critical Temperature (K) |
| $P_c$ | Critical Pressure (bar) |
| $Z_c$ | Critical Compressibility Factor |
| $V_c$ | Critical Volume ($m^3$/kmol) |
| $T_b$ | Normal Boiling Point (K) |
| $d_m$ | Dipole Moment (C·m) |
| $r_g$ | Radius of Gyration (nm) |
| $T_m$ | Melting Point (K) |
| $T_{tp}$ | Triple Point Temperature (K) |
| $P_{tp}$ | Triple Point Pressure (Pa) |
| $M_v$ | Molar Volume ($m^3$/kmol) |
| $H_f$ | Ideal Gas Heat of Formation (kJ/kmol) |
| $G_f$ | Ideal Gas Gibbs Energy of Formation (kJ/kmol) |
| $S_{IG}$ | Ideal Gas Absolute Entropy (kJ/(kmol · K)) |
| $H_{fus}$ | Heat of Fusion at Tm (kJ/kmol) |
| $H_{comb}$ | Standard Net Heat of Combustion (MJ/kmol) |
| $\Delta$ | Solubility parameter (kJ/$m^3$) |
| $V_{vw}$ | Van der Waals Volume ($m^3$/kmol) |
| $A_{vw}$ | Van der Waals Area ($m^2$/kmol) |
| $P_{nvap}$ | Normal Vapour Pressure (Pa) |

Figure 24 illustrates the algorithm used in process analysis step to generate all the information required to solve the synthesis problem. The algorithm also details the use of different databases, tool and methods used in this step.

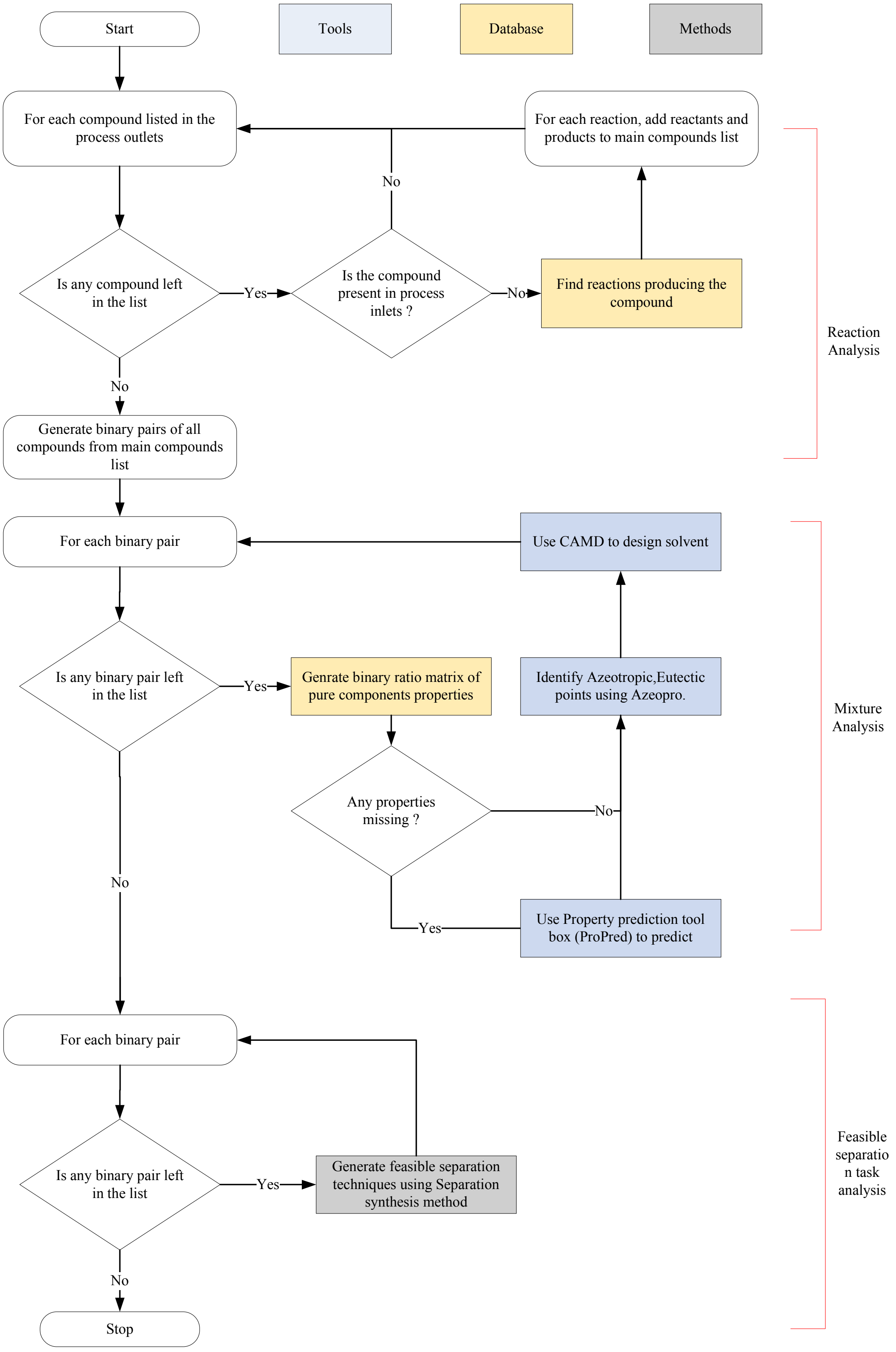


*Figure 24 : Algorithm for Problem Analysis Step*

### 3.1.3 Process-groups Selection:

The selection and initialization of the process groups is based on the analysis of the synthesis problem carried out in problem analysis step of the method. According to the process-group concept, the process-groups are component property dependent, which means the same process-group can be used to represent the operation task with different sets of components as long as it satisfies the property constraints. This step of the method involves three tasks: i) initialization of inlet and outlet process-groups, ii) selection and initialization of reaction process-groups, and iii) selection and initialization of separation process-groups.

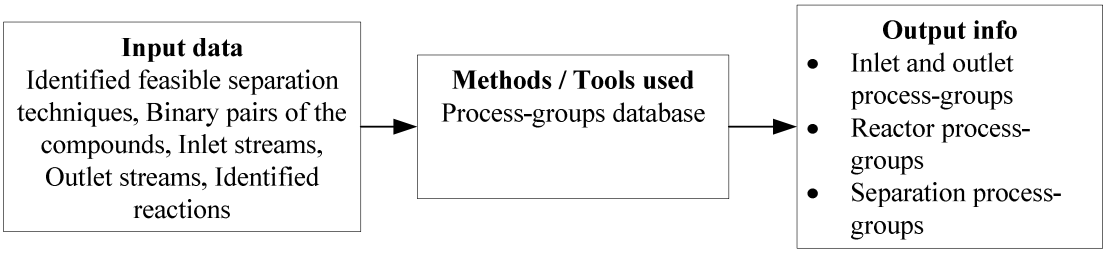


*Figure 25: Method/Tools and information flow for step 3 of the method*

1) Based on the information from inlet and outlets streams provided in the problem definition step, the inlet and outlet process-groups are selected and initialized with the corresponding components.

2) From the problem analysis step, the complete list of reactions along with chemical components involved and optional kinetic model parameters or conversion rates are available. For each reaction (or set of reactions), if the kinetic model parameters are available, a kinetic model based reactor process-group is selected; otherwise, a fixed conversion-based reactor process-group is selected. As the corresponding reaction process-groups are selected, they are initialized with the components in the reaction and the reaction data available.

3) The separation process-groups are selected from the database based on the identified feasible separation tasks during the synthesis problem analysis. For each feasible separation task identified, the corresponding process-group is selected and initialized as explained in section 2.2.2.1.

Figure 26 illustrates the algorithm used in process-group selection step to select all the process-groups and initialize the given synthesis problem with all the component combinations feasible. The algorithm also details the use of the process-groups database used in this step.

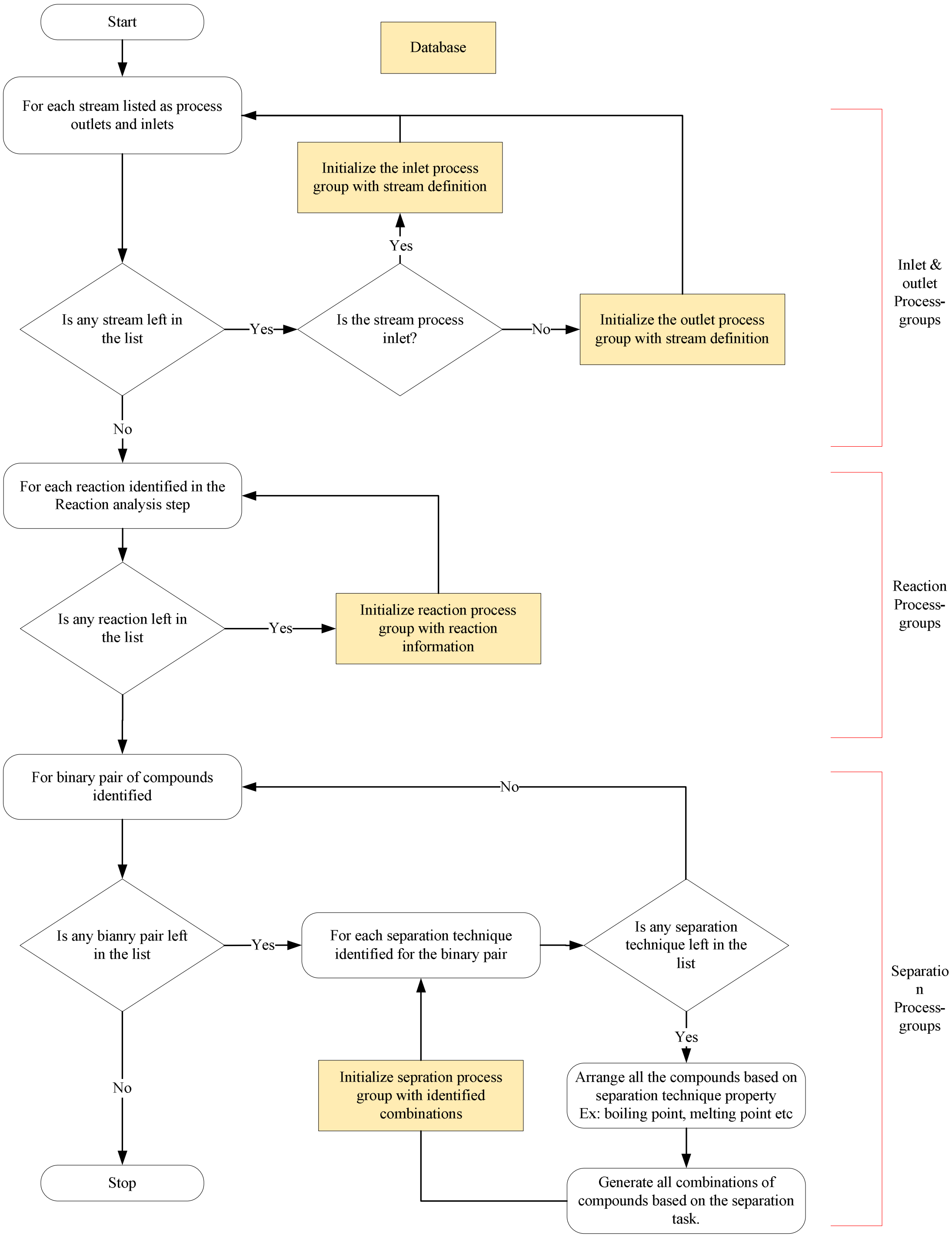


*Figure 26: Algorithm for Process-groups selection tab*

### 3.1.4 Generation of Flowsheets:

In this step, the initialized process-groups are combined according to a set of rules and specifications to generate feasible alternative flowsheet structures. Figure 27 represents the information flow for this step.

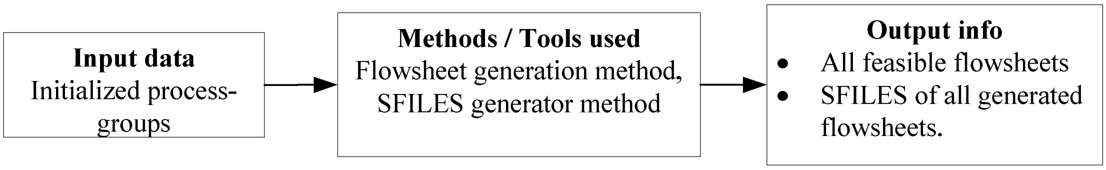


*Figure 27: Method/Tools and information flow for step 4 of the method*

This objective is achieved in two tasks.

1) **Superstructure Generation:** Flowsheet generation method is based on a combinatorial algorithm, is employed to generate all the structurally feasible flowsheet alternatives from the initialized process-groups. The method generates new flowsheet alternatives by combining process-groups according to set of connectivity rules which is explained in section 2.2.2.2. The method starts with the inlet process-groups representing the inlet streams as defined by the problem definition step and keeps on adding the process groups whose inlet connection matches with the outlet connection of the selected process-group as represented in Figure 28. Figure 28 represents superstructure of feasible alternatives for a 4-component separation synthesis problem. Where process-group "iABCD" representing the feed stream and the process-groups "oA", "oB", "oC" and "oD" are the desired product streams. Process flowsheets corresponding to different configurations, as given by the superstructure, can be represented using process-groups as shown in Figure 29.

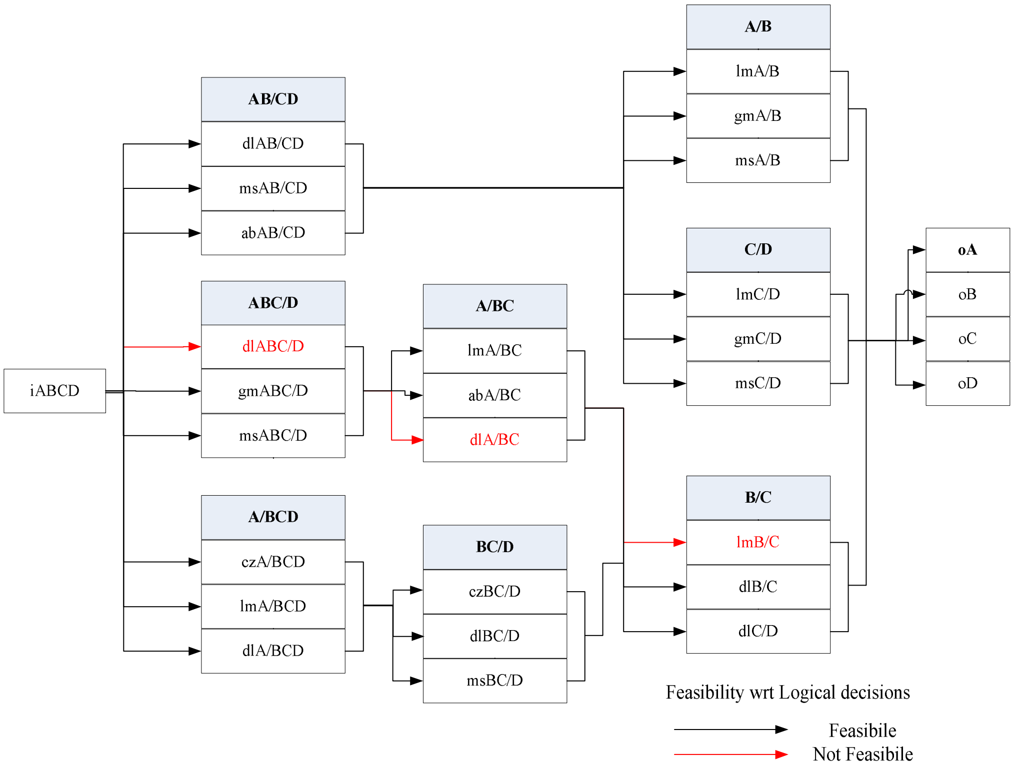


*Figure 28: Superstructure of feasible alternatives for a separation synthesis problem*

Figure 29 gives two feasible process alternatives from the generated superstructure of alternatives for the separation synthesis. In the first alternative, three distillation columns are used to separate the 4-component mixture and, in the second case, only two distillation columns and a membrane are required to achieve the synthesis task.

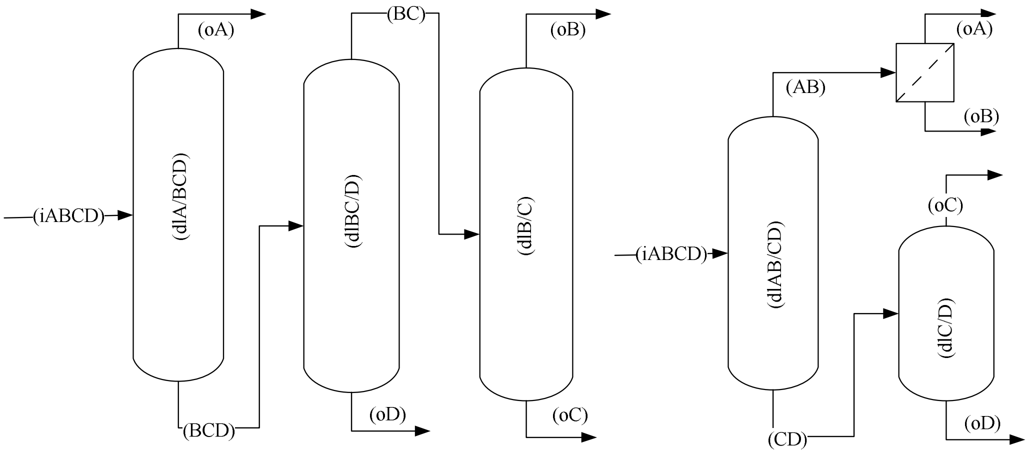


*Figure 29: Two feasible process alternatives for the separation synthesis problem*

The process-groups guarantee the recovery of the components in their outlets during the generation of the flowsheet structures. For instance, the process-group (dlBC/D) can be connected to the output of process-group (dlA/BCD) independently of the composition of the mixture of A, B, C and D entering the (dlA/BCD) process-group. In this case, the outputs of the process-group (dlA/BCD) are ensured to be, on the one hand, a mixture of B, C and D, and, on the other hand, a stream with a high purity and recovery of component A.

**Generation of SFILES:** Having a process flowsheet represented by process-groups provides the possibility to employ simple notation systems for efficient storage of structural information of all the process alternatives generated using SFILES notation as explained in section 2.2.2.3. d'Anterroches and Gani (2006) introduced the SFILES (Simplified Flowsheet Input Line Entry System) method to store the structural information of process flowsheets.

Figure 30 gives the algorithm used in this step, where flowsheets are generated from the pool of process-groups initialized for the synthesis problem and finally converted into SFILES format for efficient storage of all generated process topologies.

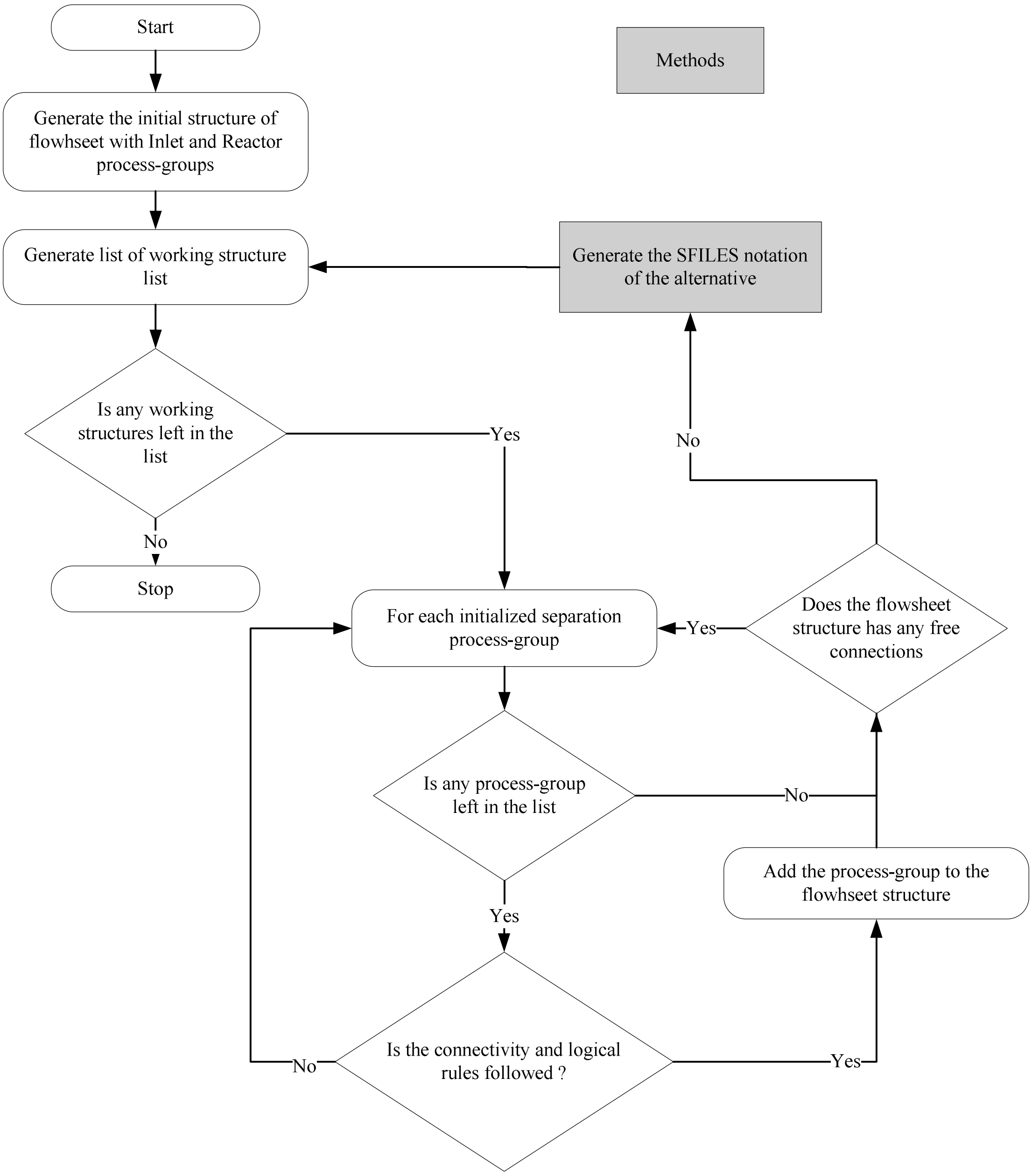


*Figure 30: Algorithm for Generation of Flowsheets Step*

### 3.1.5 Ranking of Flowsheets:

Once all the feasible process alternatives are generated for the defined synthesis problem, ranking or benchmarking of these feasible alternatives is performed to select the most promising alternatives. Ranking of the alternatives can be done based on a single property or by minimizing a weighted sum of objectives, depending upon the property targets selected during the synthesis problem definition step of the methodology. So, in this step of the method, different group contribution based flowsheets property models are used to evaluate the flowsheet properties and benchmark them accordingly. The general representation of a flowsheet group contribution based property model can be derived as shown by equation 3.1.

$$f(P) = \sum_{k=1}^{NG} pos_k * a_k \qquad (3.1)$$

Where f(*P*) is the flowsheet property function, *NG* is the number of process groups, $a_k$ is the regressed contribution of group *k*, and $pos_k$ is the topology factor

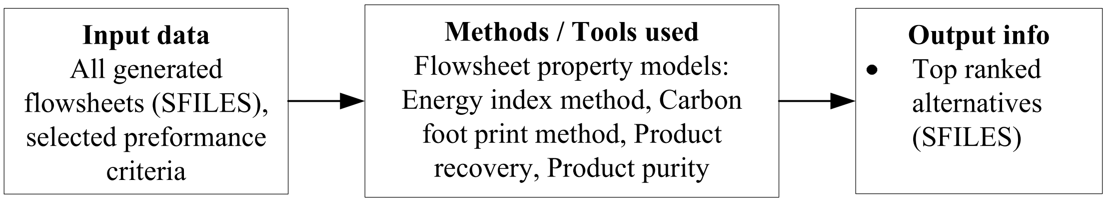


*Figure 31: Method/Tools and information flow for step 5 of the method*

Different flowsheet models are developed based on Equation 3.1, which can estimate carbon footprint, energy consumption, product recovery and purity of any process flowsheet, based on process-groups. All the models are given and explained in section 2.2.2.4. Here ranking can be done based on single property model or combination of more than one property model, based on the selected performance criteria in step 1. Figure 32 gives the algorithm used in this step, where all the process-groups present in the flowsheet are identified and the different flowsheet properties models are used to estimate the flowsheet properties.

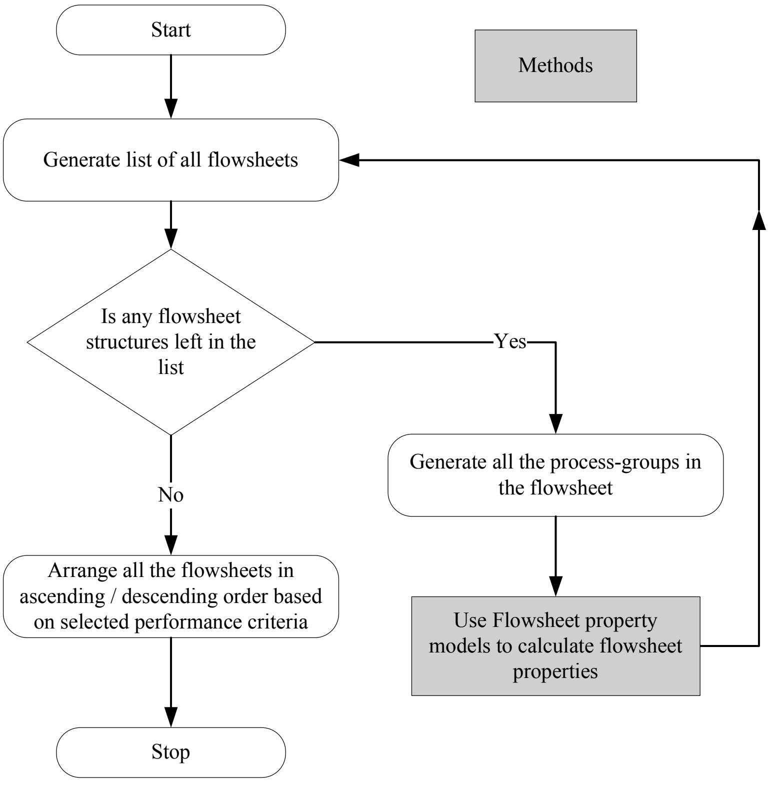


*Figure 32: Algorithm for Ranking of Flowsheets Step*

### 3.1.6 Process Design:

At this stage of the method, only the block representation of the process alternative is known. Therefore, in this step, the basic design parameters of the selected process alternatives are calculated. This step is carried out through the following two tasks: i) the resolution of the mass and energy balance through each process-group in the selected alternative, and ii) calculation of flowsheet design parameters of the process unit operations in the flowsheet structure through reverse simulation concept, as explained in section 2.2.3. Figure 33 illustrates the database and methods used in this step along with the information flow.

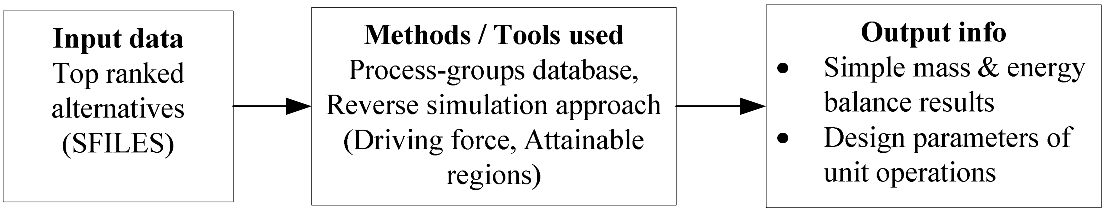


*Figure 33: Method/Tools and information flow for step 6 of the method*

**Resolution of mass & energy balance:** The mass balances for the alternatives are performed through simple models of splitters, mixers and reactors, as explained in section 2.2.3. Along with recoveries, the operating conditions, such as pressure and temperature of the outlet streams, can be estimated from the process-group information.

Parameters for simple models:

- For the reactor model, the parameters needed are conversion and stichometric coefficients, which are obtained from the selected reactor process-group.
- For splitter (separation) models, the main parameters required are the separation factors of the components present in the inlet stream. These are obtained from the definition of the process-groups. For instance, in the case of the distillation process-group, the recovery of the components lighter than the light key is equal to 100% in the overhead product and the recovery of the components heavier than the heavy key is equal to 100% in the bottom product. The recovery of the key components is greater than or equal to 99.5%. Similiarly, separation factors based on different driving forces available for each process-group are defined. For the splitter parameters for the process-groups, refer Appendix C.
- In order to solve the energy balance models, the main parameters required are temperature and composition of the stream. Similar to mass balance models, these parameters are also obtained from the process-group definition and process itself. For instance, in the case of the reactor process-group, the temperature of the outlet is set to the reaction condition, which comes from the reactor process-group definition. Similiarly, for distillation process-group, the distillate temperature is set at bubble point or, in case of non-condensables, dew point. The bottoms stream of the distillation process-group is always set at bubble point. For temperature conditions for all process-groups refer Appendix C.

Figure 34 gives the algorithm used in this step, where mass balance results are used in energy balance calculations.

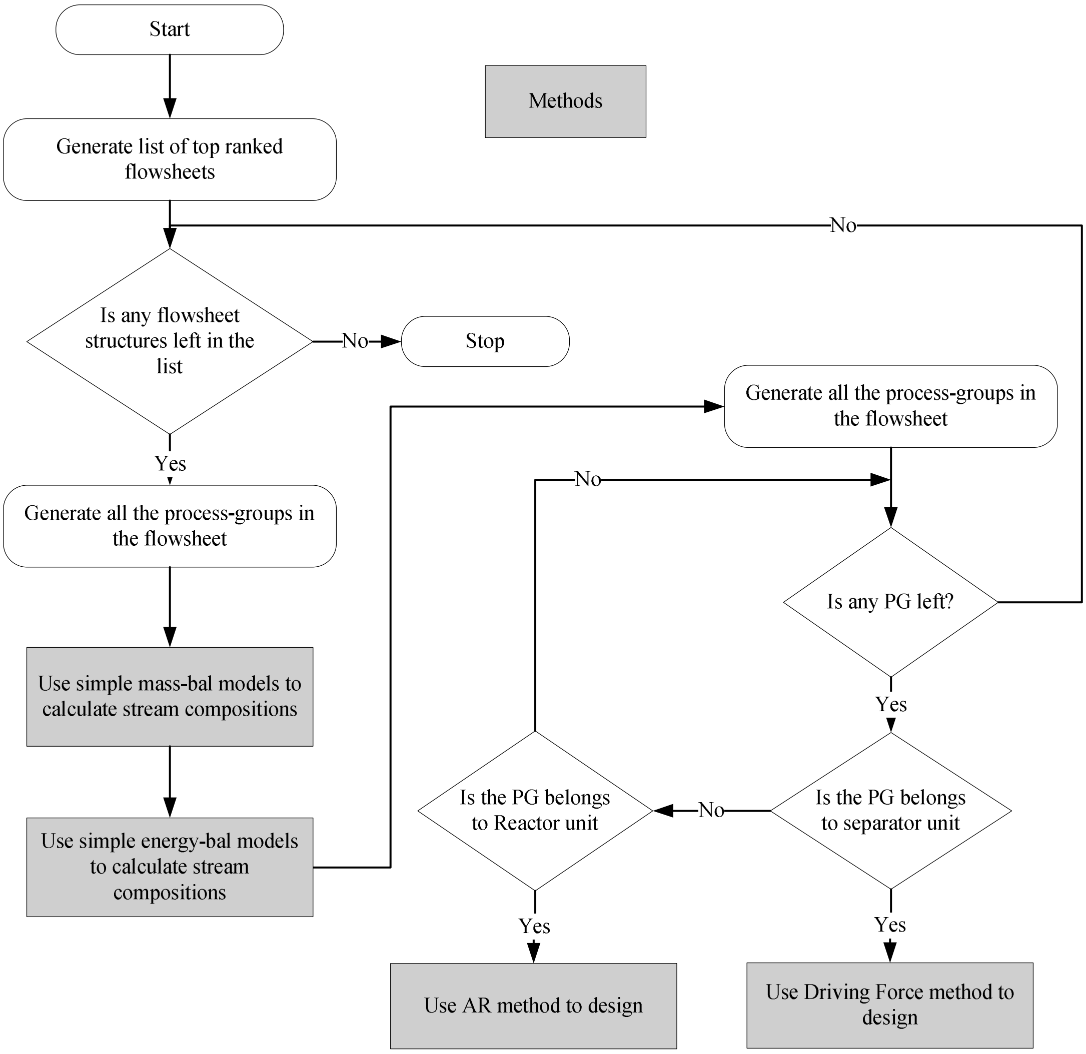


*Figure 34: Algorithm for Ranking of Process design Step*

**Process design:** The objective of this task is to calculate all the design parameters required to fully define the flowsheet for a rigorous simulation (for all the unit operations present in the flowsheet alternatives). For this, the reverse simulation method for separation process-groups (such as distillation, extractive distillation, and flash), which is based on the driving force (DF) concept introduced by Bek-Pedersen and Gani (2004), is used. The procedure to determine the design parameters of the distillation columns, in the simple distillation process groups, is as follows:

i. Given a *NC* component process group.
ii. Order the components with respect to relative volatility and identify the key components.

iii. Either from VLE calculation or experimental data, retrieve the maximum driving force between the key components $F_{Di|Max}$ and the composition of the light key at its maximum $D_x$.

iv. Based upon the process-group definition, select the recoveries of the key components, 99.5% in this case.

v. If the inlet composition is between the requested purities for the bottom and top product, the ideal number of stages $N_{ideal}$ for the column is retrieved from the pre-calculated values Table A1.1 (Appendix A).

vi. Feed plate location of the column is calculated as $N_F = (1 - D_x)N_{ideal}$.

Similarly, the reverse simulation for the kinetic model based reactor process-group is based on the attainable region theory, as explained in section 2.2.3.

### 3.1.7 Rigorous Simulation:

At this step of the method, all the necessary information to perform the final verification through rigorous simulation is available. Rigorous simulators like PROII, ICASSim (R Gani et al. 1997; R Gani 2002) or any other process simulator can be used simulate and verify the design and performance of the selected designs. The rigorous simulation is set up by using the results from different steps from the method. The process-groups definitions will be used to select the type of unit operation and determine the the specifications to satisfy the degrees of freedom. For example, in order to set up a rigorous reactor model, all the needed variables are given by the reactor process-group:

- Temperature, pressure of the reactor
- Reactions
- Kinetics/ conversions

Similiary, to set up a rigorous distillation column, the necessary variables needed to specified are:

- Specifications on light and heavy key (obtained from process-group definition)
- Specification on type of condenser (obtained from process-group definition)
- Number of stages (obtained from Process design step of method)
- Feed stage location (obtained from Process design step of method)

Table 12 gives the information on the rigorous model used for the process-group in the selected alternative, along with the specifications/variables that are required to satisfy the degrees of freedom.

*Table 12: Setting up rigorous models in commercial simulator*

| **Process-group** | **Specifications** | **Simulator model used** |
|---|---|---|
| Reactor PG | Temperature, Pressure, reaction data based on reactor process-group definition | Kinetic/conversion reactor |
| Distillation PG | Recovery specifications and condenser type based on process-group definitions (driving force available). Number of stages and feed location | Rigorous distillation column |
| Azeotropic distillation PG | Recovery specifications and condenser type based on process-group definitions (solvent free driving force, driving force for recovery column). Number of stages and feed location | Two rigorous distillation columns and decanter |
| Crystallization PG | Recovery specifications and outlet temperature based on SLE plot. | Stream calculator with basic model based on SLE analysis |
| Extractive distillation PG | Recovery specifications and condenser type based on process-group definitions (solvent free driving force, driving force for recovery column). Number of stages and feed location | Two rigorous distillation columns |
| Flash PG | Recovery specifications based on process-group definitions ( driving force available) | Flash |
| Gas membrane PG | Recovery specifications based on selectivity/default values from process-group definition | Stream calculator with basic model based on selectivity |
| Liquid-liquid extraction PG | Recovery specifications and condenser type based on process-group definitions (solvent free driving force, driving force for recovery column) | one liq-liq column, one rigorous distillation column |
| Liquid membrane PG | Recovery specifications based on selectivity/default values from process-group definition | Stream calculator with basic model based on selectivity |
| Molecular sieve adsorption PG | Recovery specifications based on selectivity/default values from process-group definition | Stream calculator with basic model based on selectivity |
| Pervaporation PG | Recovery specifications based on selectivity/default values from process-group definition | Stream calculator with basic model based on selectivity |

The results of the rigorous simulation (stream summary, equipment sizing, energy balance etc.) are used to perform economic, sustainability and life cycle analyses.

**Economic Analysis:** This analysis is performed using software tool, ECON (Kalakul et al. 2014), which is based on cost models from Peters et al. (1991) and Biegler et al. (1998). The outcome of this analysis includes capital and utility costs for each unit operation, total operational cost and profit, which is defined as difference between sale of products and total operating cost. The main input for this analysis includes mass and energy balance results from the rigorous simulation. Apart from this, pricing details for different utilities, raw materials and products in the synthesis problem are used by ECON to estimate the capital and utility costs associated with the process. Economical evaluation, as shown in Figure 35, will identify the unit operations with the highest operational costs, and hence point towards the unit operations where greater savings, in terms of energy costs, can be achieved.

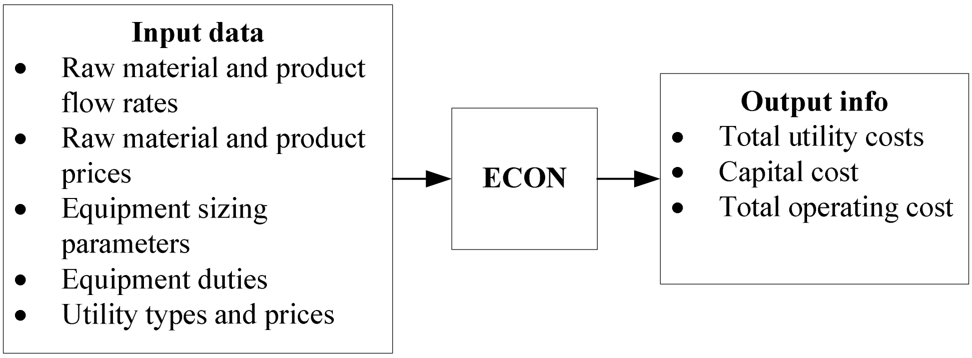


*Figure 35: Information flow associated with Economic analysis*

**Sustainability Analysis:** This analysis is based on an indicator-based methodology (Carvalho, Gani, and Matos 2008), which identifies critical flow paths within the process. Here analysis is done on both open (where a chemical species enters and leaves the process) and closed paths (like recycle loops where mass and energy are recycled without going out of the process). The main indicators, which are estimated, are: material value added (MVA), energy and waste cost (EWC), total value added (TVA).

1) Material Value Added Indicator: This reflects the value added between the entrance and exit (open path) of a given chemical species in a given process stream (path). Positive value for this indicator means that the component has increased its value in this path and negative values indicate that the component has lost its value in this path and, therefore, point to potential for improvements.

2) Energy and Waste Cost Indicator: This indicator provides the estimate on the total cost associated with energy and compound treatment cost in the flow paths. This indicator is estimated for both open and closed paths in the process. The indicator represents the maximum theoretical amount of energy that can be saved, so the paths with high values are targeted in order to improve the process.

3) Total Value Added Indicator: The indicator describes the economic impact of a compound in a path. It is the difference between MVA and EWC. Therefore, negative

values of this indicator show high potential for improvement related to the decrease in the variable costs.

The model-based tool, SustainPro (Carvalho, Matos, and Gani 2013), is used to calculate the above explained indicators. Figure 36 gives the details of all the information required for SustainPro to calculate the three indicators.

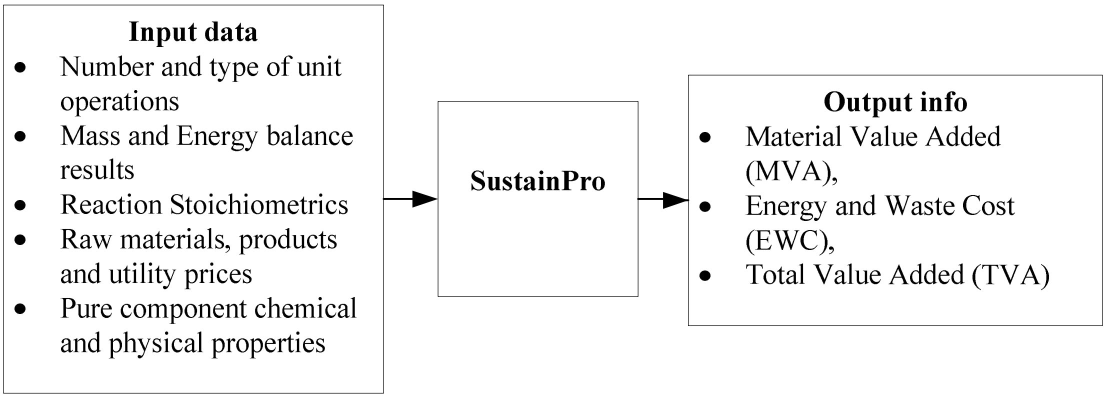


*Figure 36: Information flow associated with Sustainability analysis*

**Life Cycle Analysis:** This analysis is used to estimate environmental assessment of the selected process alternative. This analysis is carried out through LCSoft (Kalakul et al. 2014) that helps to quantify potential environmental impacts of chemical process. The main factors which are estimated in this analysis are:

i. Carbon Footprint
ii. HTPI : Human Toxicity Potential by Ingestion
iii. HTPE: Human Toxicity Potential by Exposure
iv. GWP: Global Warming Potential

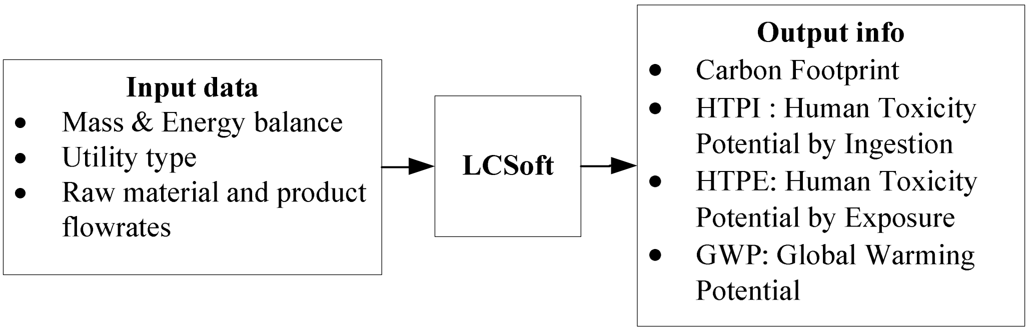


*Figure 37: Information flow associated with Life Cycle analysis*

Based on the results from the three analyses, process hotspots are identified using Table 13. The most sensitive process hotspots are translated and selected as design targets using Table 14. Matching of these design targets minimizes/eliminates the process hot-spots and, therefore, generates non-tradeoff innovative process designs.

*Table 13: Translation of economic, sustainability and LCA analyses into process hot-spots. MVA-mass value added, EWC-Energy to waste cost, CO2 eq-carbon footprint, EI-Environmental impact. Adopted from Babi 2014*

| **Indicator values** | **Base Case property** | **Reason** | **Identified Process hot-spot** |
|---|---|---|---|
| 1. Raw material recycle/cost<br>2. MVA | Un-reacted raw materials | Equilibrium reaction | 1. Activation problems<br>2. Limiting equilibrium/raw material loss<br>3. Contact problems of raw materials/limited mass transfer<br>4. Limited heat transfer |
| 1. Utility cost<br>2. EWC<br>3. CO2 equivalent | Hrxn Reactor cooling | Exothermic reaction - | Highly exothermic reaction |
| 1. Utility cost<br>2. EWC<br>3. CO2 equivalent | Hrxn Reactor heating | Endothermic reaction | Highly Endothermic reaction |
| 1. Utility cost<br>2. Capital cost | Reactor operating conditions | Temperature and pressure operating window for the reactor | 1. Explosive mixture<br>2. Product degradation by temperature |
| 1. Product sale<br>2. EI | Formation of byproduct(s) | NOP=number of desired products plus number of undesired products | Formation of undesired side-products |
| 1. Utility cost<br>2. MVA<br>3. EWC<br>4. CO2 equivalent<br>5. EI | Un-reacted raw materials and products recovery | 1. Presence of azeotrope(s)<br>2. High energy usage heating and/or cooling | 1. Azeotrope<br>2. Difficult separation:<br>3. low driving force<br>4. High energy consumption and/or demand |

*Table 14: Identified design targets from the identified process hot-spots. Adopted from (Babi 2014)*

| **Process hot-spots** <br> **Design target** | Activation problems | Limiting equilibrium | Limited heat transfer | Degradation by temperature | Formation of undesired side-products | Azeotrope | Difficult separation due to low driving force | High energy consumption /demand |
|---|---|---|---|---|---|---|---|---|
| Increase raw material conversion | | | | | | | | |
| Reaction-use of a solvent | * | * | | | * | * | * | * |
| Reaction-new | * | * | | | * | * | * | * |
| Reduce raw material loss | * | * | * | | * | * | * | * |
| Reduce product loss | | | | * | | * | * | * |
| Reduce by-product formation | | | | | | * | * | * |
| Reduce utility cost | | | * | * | | * | * | * |
| Unit operations reduction | * | * | * | * | * | * | * | * |
| Product purity | * | * | * | * | * | * | * | * |
| Production target | * | * | * | * | * | * | * | * |
| Waste minimization | * | * | * | * | * | * | * | * |

### 3.1.8 Innovative Designs:

This is an optional step in the method, where based on identified design targets, different strategies/methods are applied individually to the selected alternative to target the hot spots for overall process improvement.

#### 3.1.8.1 Simultaneous Process Optimization and Heat Integration:

Duran and Grossmann (1986b) propose a strategy of simultaneous process optimization and heat integration is applied to the analyzed base case design, to target process hotspots involving raw material losses and high operational costs. Process optimization generally involves determination of optimal operating conditions, determination of optimal design parameters, etc., while heat integration involves minimizing utility consumption and maximizing heat recovery of the process. Since both the problems are interlinked, one has to solve both problems simultaneously, in order to account for the interactions between chemical process and heat integration network.

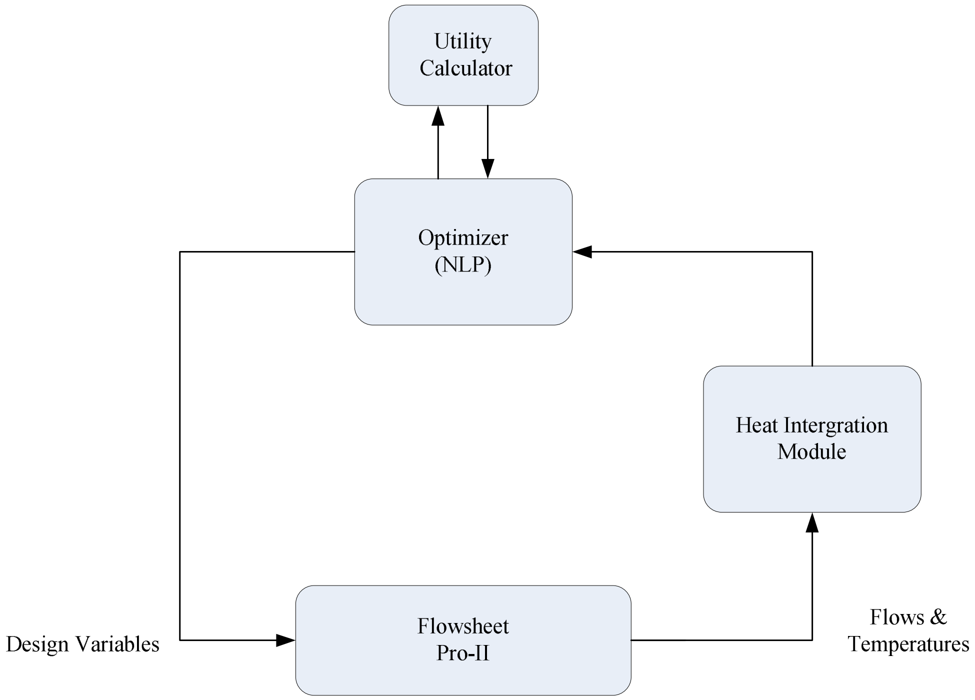


*Figure 38: Strategy for Simultaneous Process Optimization and Heat Integration*

Figure 38 gives the strategy for solving the simultaneous optimization problem, where:

- The process simulator is used to calculate process information.
    1. For example, raw material consumption rates, product rates and equipment sizes from process inputs.
- The heat integration module gets unit information and process stream information from the simulator.
    1. For example, heating and cooling unit requirements.
    2. Flow rates, temperatures and stream enthalpies.

- Based on this information, the integration module calculates the minimum utility consumption (or utility cost) and minimum number of heat exchangers.
- The optimizer module uses the information from both process simulator and heat integration module to minimize the total cost.

In this method, the heat integration module is based on the condensed LP transshipment model for calculating minimum utility consumption or cost as explained in section 2.2.6. The generalized form for the combined simultaneous problem can be defined as:

Given a process flowsheet which involves set of hot and cold streams

$$\text{Min Cost} = \text{Operation Cost} + \text{Utility Cost} \tag{3.2}$$

or

$$\text{Max Profit} = \text{Revenue} - \text{Cost} \tag{3.3}$$

Subject to Process flowsheet constraints

*Min utility Cost -> Utility loads*

### 3.1.8.2 Hybrid Separations:

In this strategy, a generalized method based on Tula et al. (2016) for synthesis-design of hybrid distillation-membrane based separation systems is applied to replace the distillation columns in the base case design with a hybrid distillation-membrane system to reduce the operational cost substantially. This algorithm is based on the concept as explained in section 2.2.7, where it was shown that 30-50 % of energy savings can be achieved for a distillation column by replacing the less efficient region of the distillation with membrane separation technique.

*Step-by-step algorithm:*

This algorithm solves the following problem: given a mixture to be separated into two products in a distillation column, determine a hybrid separation scheme where distillation is used for part of the separation and a membrane module is used for the part where distillation operation is replaced by a non-thermal operation. The single distillation scheme for a simple distillation column with one feed and two products streams is shown in Figure 39.

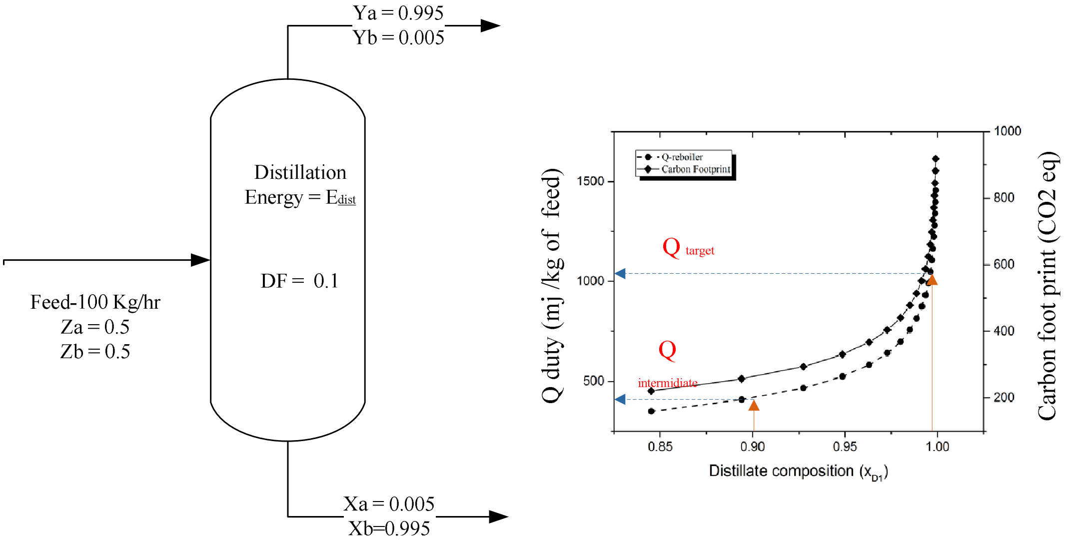


*Figure 39: Simple Distillation task with reboiler duty analysis*

Step 1: Calculate the driving force diagram for the given separation task. For a multi-component mixture, select the two key components which define the spilt and use them as the binary mixture to generate the driving force plot.

Step 2: Using the calculated driving force and knowledge base of pre-calculated values for reboiler-condenser duties as a function of product purities, identify $Q_{target}$ and $Q_{intermediate}$.

Step 3: Estimate the potential energy savings $Q_{savings}$ using equation 2.39.

Step 4: Perform simulation of the hybrid process to verify the total energy savings.

Step 5: Calculate the membrane area required for the separation to calculate the additional capital cost.

# 4

# PROTOTYPE: SUSTAINABLE PROCESS SYNTHESIS SUITE

In this chapter, the prototype implementation of developed sustainable process synthesis-design and analysis method is presented. This chapter also includes the software architecture of the computer-aided method, along with integration of various methods and tools developed within the research group. This presentation also includes the screenshots of the prototype tool itself.

## 4.1 ARCHITECTURE OF PROCESS SYNTHESIS SUITE

The architecture for the computer-aided tool for performing process synthesis-design and analysis in order to achieve sustainable design, is presented in Figure 40. As shown in the previous chapter, the framework requires integration of different tools, methods, models and database libraries to solve the synthesis problem. The prototype was completely built in the visual C# environment, using the concepts of object oriented programming. The software itself is developed, keeping in mind the present and future integration needs to further expand the capabilities of the tool. On the highest level of the tool, it has 6 different component structures, which are connected to the main user interface, which interact to provide sufficient information to solve the synthesis-design problem.  The six components and their importance are explained below.

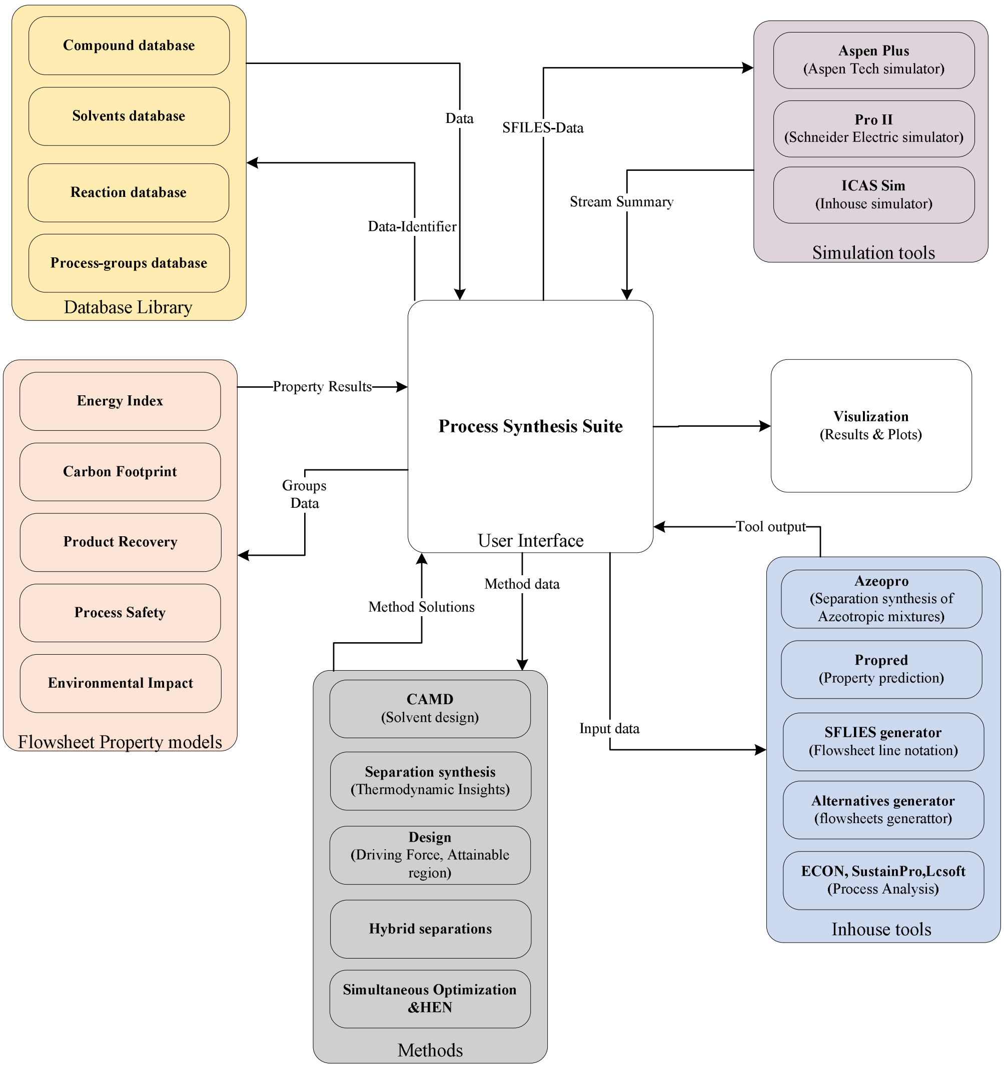


*Figure 40: High level architecture for Process Synthesis Suite*

**Database Library:**

This component of the software facilitates all the storing, retrieval and addition of information.

1) Compound database: This database library consists of all the chemical species, their pure component properties, and other model parameters, to calculate other secondary properties of nearly 15000 chemicals. This database also provides the structure information of the compounds, along with interaction parameters used in thermodynamic models to generate vapor-liquid, liquid-liquid and solid-liquid equilibrium data.

2) Solvents database: This manages the information of various industrial solvents along with binary solubility data with respect to chemicals.

3) Reaction database: This gives access to the kinetic parameters, conversions and stoichiometric data for more than 100 chemical systems. Reaction data can be

updated/modified using the tool interface, while defining the synthesis problem. New reaction data can also be added to the database from the user interface.

4) Process-Groups database: This represents digitalized information of different process-groups, their properties, connectivity rules and other information, which are used in the tool to generate alternatives.

**Simulation Tools Library:**

This part of the software facilitates the wrapper classes required to interact with simulation software for rigorous simulation of the flowsheet alternatives generated.

1) Aspen Plus: This object directly creates an aspen file of the entire flowsheet. The interaction between the tool and Aspen is made possible because of the SFILES representation of the flowsheet, which has the information of the process flow diagram and design information from the design and analysis step.

2) ProII: This object creates a ProII simulation file of the process alternative and, using ProII's external call object, it can invoke the simulation tool directly from the user interface.

3) ICASSim: This facilitates the interaction between the synthesis tool and ICASSim, which is our in-house rigorous steady state simulator.

**Flowsheet Property Model Library:**

This part of the software connects the property models library to the synthesis tool, which estimates the properties of the entire flowsheet that can be used to benchmark the alternatives.

1) Energy Index: Estimates the energy of the entire flowsheet as a function of the process group and its driving force.

2) Carbon Footprint: Calculates the total carbon foot print of the entire flowsheet in terms of $CO_2$ equivalents.

3) Product Recovery: This model estimates the percent of the product that is recovered as the main product from the total product produced in the reactor process-group.

4) Process Safety: This model estimates the process safety of the generated alternatives. The model is based on a scoring system which takes in consideration the maximum pressures and temperatures attained in the process.

5) Environmental Impact: Different environmental indicators are calculated for selected alternatives based on mass resolution results and corresponding chemical species impact factors.

**Methods Library:**

This part of the software has the methods library which is used during the synthesis and design problem to solve sub-problems or to generate data required to solve the problem.

1) CAMD: computer aided molecular design method is used to design molecules, especially solvents, that can be used in the process having specific pure component and mixture properties. This is used in designing solvents for extractive, azeotropic distillation and liquid–liquid extraction processes having specific characteristics with respect to the process.
2) Separation synthesis: This method is based on thermodynamic insights to generate the separation techniques that are feasible to carry out a separation task, which forms the basis for process-group selection and initialization.
3) Design: Calculates all the design parameters required to fully define the flowsheet for a possible rigorous simulation using concepts of driving force and attainable region.
4) Hybrid separations: This method is used to synthesize and design hybrid systems involving distillation and membrane modules to replace distillation tasks in the selected alternative.
5) Simultaneous Optimization and Heat Integration: This method is used to formulate the simultaneous process optimization and heat integration problem, based on the selected alternative and process analysis.

**Tools Library:**

This part of the software has a library of wrapper classes for different in-house tools, which are used during the synthesis and design problem to generate results at various levels of the problem solution.

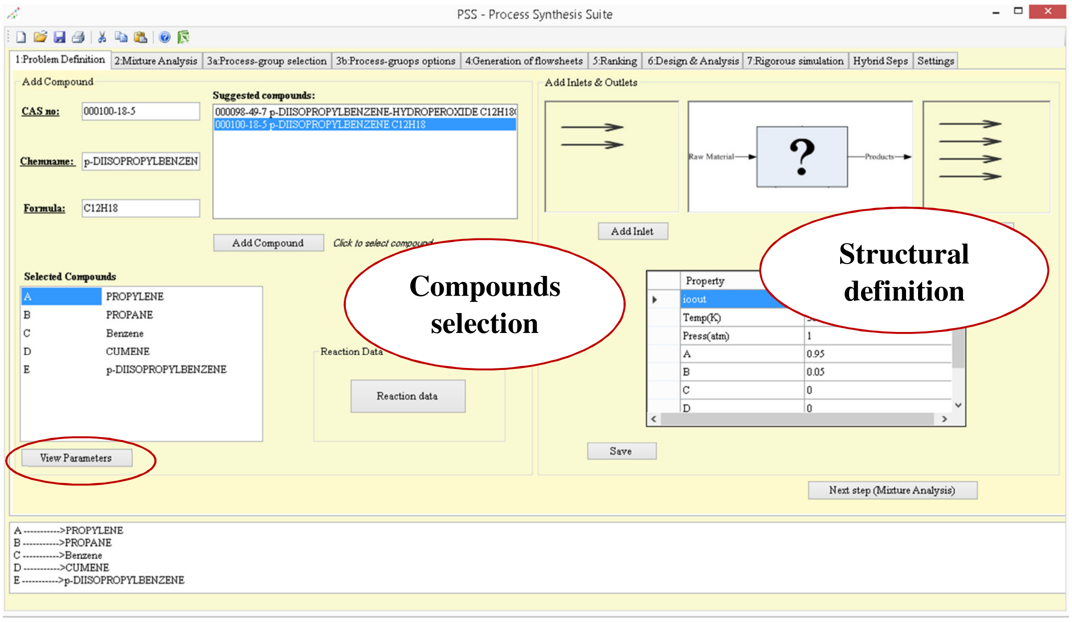
1) Azeopro: a computer aided tool based on a hybrid approach of database search and calculations to identify azeotropes and provide potential solutions to separate them using azeotropic distillation, extractive distillation and liquid-liquid extraction separation techniques.
2) ProPred: the property prediction tool of ICAS package, which uses molecular structure as the input to estimate pure component properties and environmental related properties using group contribution approach.
3) SFILES generator: the method used to generate the flowsheet line notation for all the alternatives generated so that saving, retrieving and passing on of process flow diagram is efficient.
4) Alternatives Generator: a method based on a combinatorial approach to generate process alternatives by combining initialized process-groups using connectivity rules.

## 4.2 IMPLEMENTATION OF PROCESS SYNTHESIS SUITE

The main interface of the prototype has been divided into different tabs dedicated to each step of the framework.

### 4.2.1 Problem Definition Tab:

This illustrates the first step in the method; the user interface for this tab has two sub-parts. In the left sub-part, the interface is linked to compound database where the user needs to select the compounds applicable for the synthesis problem as shown in Figure 41. The pure component properties of the selected compounds can be visualized through the "view parameters" button. On the right top part of the window, the user provides the structural definition of the problem by adding required number of inlet and outlet streams, along with stream composition, temperature and pressure of the added streams.



**CAS no:** 000100-18-5

**Chemname:** p-DIISOPROPYLBENZEN

**Formula:** C12H18

**Suggested compounds:**

000098-49-7 p-DIISOPROPYLBENZENE-HYDROPEROXIDE C12H18
000100-18-5 p-DIISOPROPYLBENZENE C12H18

**Selected Compounds**

| | |
|---|---|
| A | PROPYLENE |
| B | PROPANE |
| C | Benzene |
| D | CUMENE |
| E | p-DIISOPROPYLBENZENE |

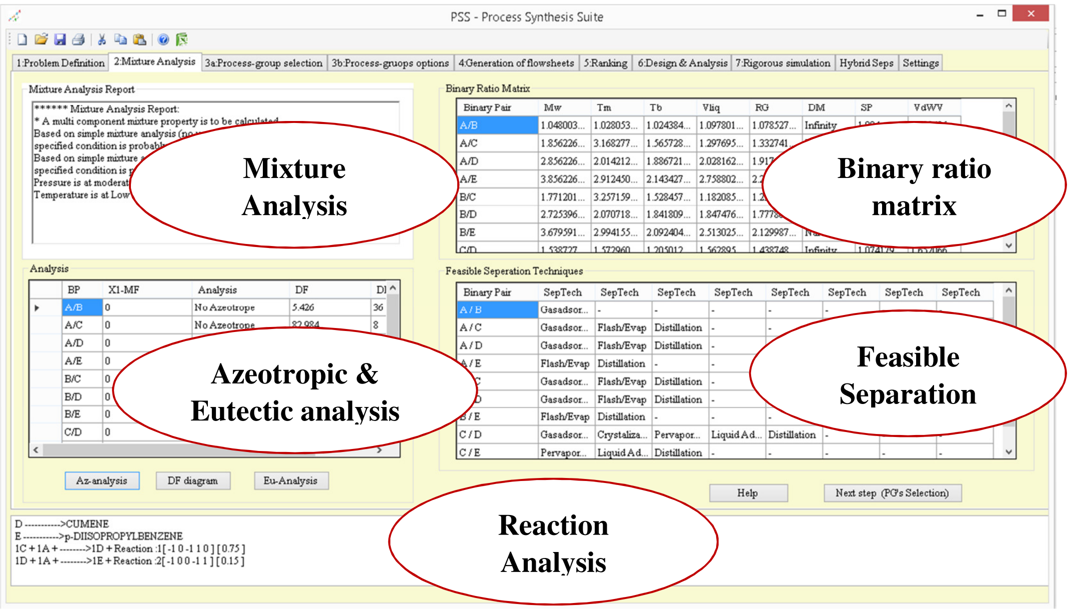
| Property | |
|---|---|
| iooout | |
| Temp(K) | [illegible] |
| Press(atm) | 1 |
| A | 0.95 |
| B | 0.05 |
| C | 0 |
| D | 0 |

```
A ----------->PROPYLENE
B ----------->PROPANE
C ----------->Benzene
D ----------->CUMENE
E ----------->p-DIISOPROPYLBENZENE
```

*Figure 41: Problem Definition tab of Process Synthesis Suite*

### 4.2.2 Analysis Tab:

In this tab, results from reaction, mixture and feasible separation task analysis are visualized in the form of tables to the user. The reactions, along with the reaction data like stoichiometric coefficients, conversion, etc. applicable for the given synthesis problem, are shown at the bottom of the window as shown in Figure 42. Azeotropic analysis results also include estimation of maximum driving force available for separation of every binary pair present in the system, including the composition pertaining to the azeotrope, etc. The feasible separation techniques results table can be edited by the user to include separation techniques, which are not selected by the separation synthesis method for a given binary pair.



Mixture Analysis Report

****** Mixture Analysis Report:
* A multi component mixture property is to be calculated
Based on simple mixture analysis (no
specified condition is probabl
Based on simple mixture a
specified condition is p
Pressure is at moderat
Temperature is at Low

Binary Ratio Matrix

| Binary Pair | Mw | Tm | Tb | Vliq | RG | DM | SP | VdWV |
|---|---|---|---|---|---|---|---|---|
| A/B | 1.048003... | 1.028053... | 1.024384... | 1.097801... | 1.078527... | Infinity | | |
| A/C | 1.856226... | 3.168277... | 1.565728... | 1.297695... | 1.332741... | | | |
| A/D | 2.856226... | 2.014212... | 1.886721... | 2.028162... | 1.917 | | | |
| A/E | 3.856226... | 2.912450... | 2.143427... | 2.758802... | 2.2 | | | |
| B/C | 1.771201... | 3.257159... | 1.528457... | 1.182085... | 1.2 | | | |
| B/D | 2.725396... | 2.070718... | 1.841809... | 1.847476... | 1.7778 | | | |
| B/E | 3.679591... | 2.994155... | 2.092404... | 2.513025... | 2.129987... | N | | |
| C/D | 1.538727 | 1.572960 | 1.205012 | 1.562895 | 1.438748 | Infinity | 1.074179 | |

Analysis

| | BP | X1-MF | Analysis | DF | DI |
|---|---|---|---|---|---|
| ▸ | A/B | 0 | No Azeotrope | 5.426 | 36 |
| | A/C | 0 | No Azeotrope | 82.984 | 8 |
| | A/D | 0 | | | |
| | A/E | 0 | | | |
| | B/C | 0 | | | |
| | B/D | 0 | | | |
| | B/E | 0 | | | |
| | C/D | 0 | | | |

Feasible Seperation Techniques

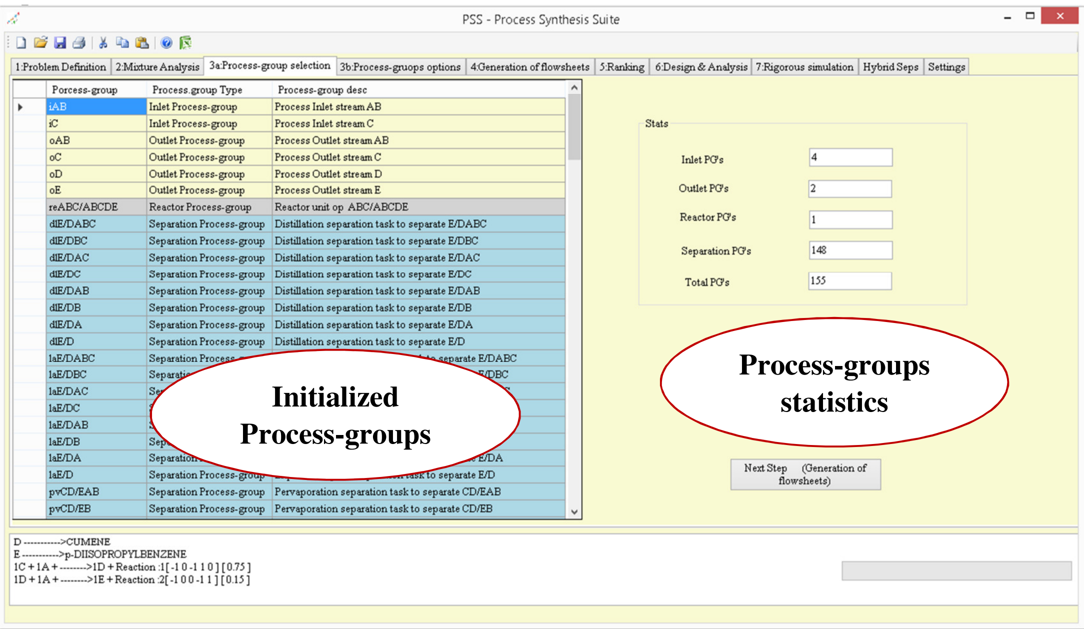
| Binary Pair | SepTech | SepTech | SepTech | SepTech | SepTech | SepTech | SepTech | SepTech |
|---|---|---|---|---|---|---|---|---|
| A / B | Gasadsor... | - | - | - | - | - | | |
| A / C | Gasadsor... | Flash/Evap | Distillation | - | - | | | |
| A / D | Gasadsor... | Flash/Evap | Distillation | - | | | | |
| A / E | Flash/Evap | Distillation | - | - | | | | |
| C | Gasadsor... | Flash/Evap | Distillation | - | | | | |
| D | Gasadsor... | Flash/Evap | Distillation | - | | | | |
| B / E | Flash/Evap | Distillation | - | - | - | | | |
| C / D | Gasadsor... | Crystaliza... | Pervapor... | Liquid Ad... | Distillation | - | | |
| C / E | Pervapor... | Liquid Ad... | Distillation | - | - | - | - | - |

D ----------->CUMENE
E ----------->p-DIISOPROPYLBENZENE
1C + 1A + -------->1D + Reaction :1[ -1 0 -1 1 0 ] [ 0.75 ]
1D + 1A + -------->1E + Reaction :2[ -1 0 0 -1 1 ] [ 0.15 ]

Figure 42: Analysis tab of Process Synthesis Suite

### 4.2.3 Process-groups Selection Tab:

As shown in Figure 43, the user will have access to all the initialized process-groups for the synthesis problem in this tab. The section also gives the statistics of different types of selected process-groups, which includes the number of inlet, outlet, reactor and separation process-groups.



| | Porcess-group | Process.group Type | Process-group desc |
|---|---|---|---|
| ▸ | iAB | Inlet Process-group | Process Inlet stream AB |
| | iC | Inlet Process-group | Process Inlet stream C |
| | oAB | Outlet Process-group | Process Outlet stream AB |
| | oC | Outlet Process-group | Process Outlet stream C |
| | oD | Outlet Process-group | Process Outlet stream D |
| | oE | Outlet Process-group | Process Outlet stream E |
| | reABC/ABCDE | Reactor Process-group | Reactor unit op ABC/ABCDE |
| | dlE/DABC | Separation Process-group | Distillation separation task to separate E/DABC |
| | dlE/DBC | Separation Process-group | Distillation separation task to separate E/DBC |
| | dlE/DAC | Separation Process-group | Distillation separation task to separate E/DAC |
| | dlE/DC | Separation Process-group | Distillation separation task to separate E/DC |
| | dlE/DAB | Separation Process-group | Distillation separation task to separate E/DAB |
| | dlE/DB | Separation Process-group | Distillation separation task to separate E/DB |
| | dlE/DA | Separation Process-group | Distillation separation task to separate E/DA |
| | dlE/D | Separation Process-group | Distillation separation task to separate E/D |
| | laE/DABC | Separation Process | to separate E/DABC |
| | laE/DBC | Separati | E/DBC |
| | laE/DAC | Se | |
| | laE/DC | | |
| | laE/DAB | | |
| | laE/DB | Sep | |
| | laE/DA | Separation | E/DA |
| | laE/D | Separation Process-group | task to separate E/D |
| | pvCD/EAB | Separation Process-group | Pervaporation separation task to separate CD/EAB |
| | pvCD/EB | Separation Process-group | Pervaporation separation task to separate CD/EB |

Stats

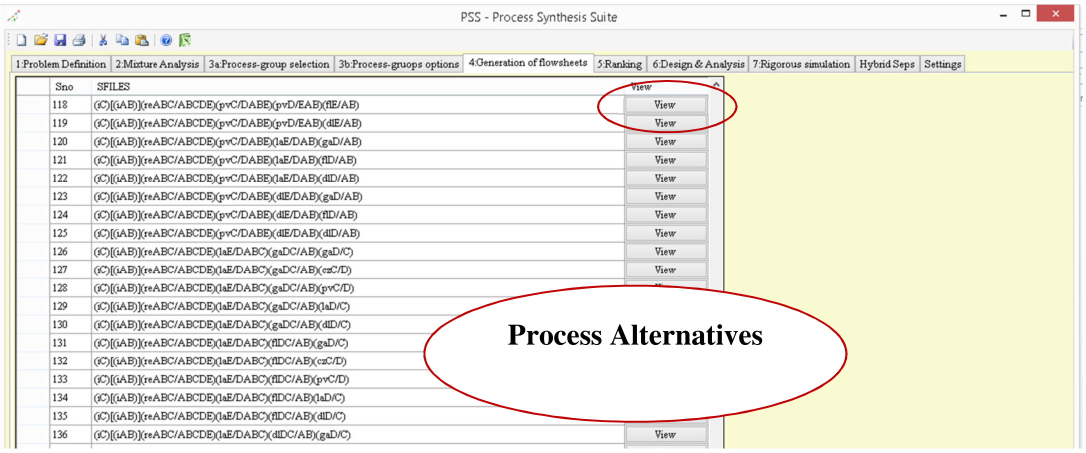
| | |
|---|---|
| Inlet PG's | 4 |
| Outlet PG's | 2 |
| Reactor PG's | 1 |
| Separation PG's | 148 |
| Total PG's | 155 |

D ----------->CUMENE
E ----------->p-DIISOPROPYLBENZENE
1C + 1A + -------->1D + Reaction :1[ -1 0 -1 1 0 ] [ 0.75 ]
1D + 1A + -------->1E + Reaction :2[ -1 0 0 -1 1 ] [ 0.15 ]

Figure 43: Process-group selection tab of Process Synthesis Suite

### 4.2.4 Generation of Flowsheets Tab:

In this tab, all the generated alternatives are shown in the form of SFILES to the user, as shown in Figure 44. Here the user has the option to visualize the block representation of the alternative by selecting the "view" button. The flowsheet alternatives are generated using the alternatives generator method, using process-groups as explained in section 2.2.2.2.

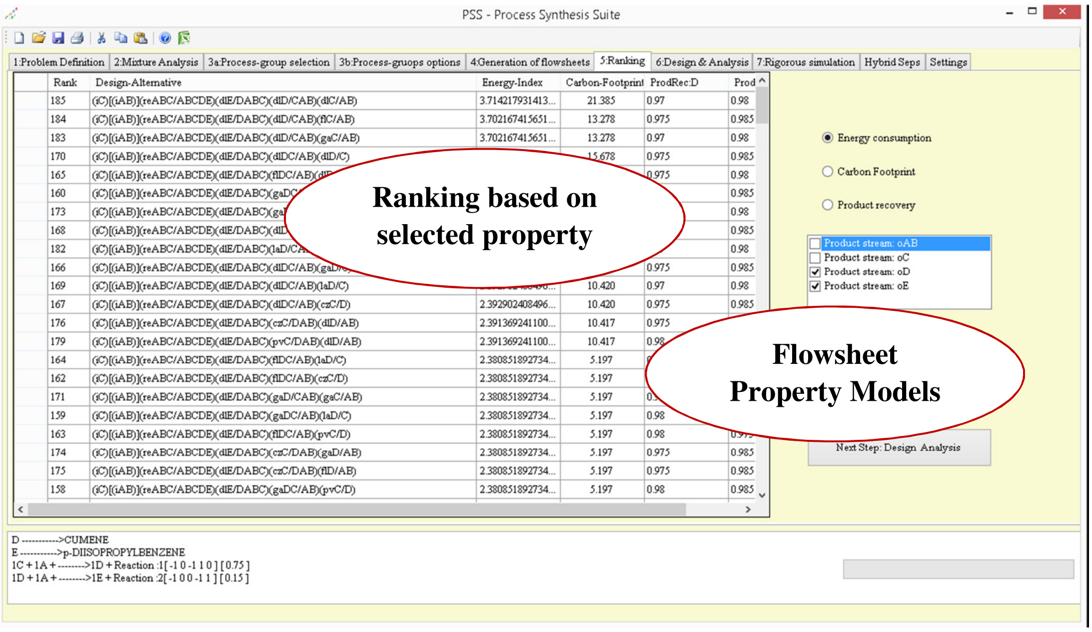


| Sno | SFILES | View |
|---|---|---|
| 118 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(pvD/EAB)(flE/AB) | View |
| 119 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(pvD/EAB)(dlE/AB) | View |
| 120 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(gaD/AB) | View |
| 121 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(flD/AB) | View |
| 122 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(dlD/AB) | View |
| 123 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(gaD/AB) | View |
| 124 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(flD/AB) | View |
| 125 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(dlD/AB) | View |
| 126 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(gaD/C) | View |
| 127 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(czC/D) | View |
| 128 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(pvC/D) | |
| 129 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(laD/C) | |
| 130 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(dlD/C) | |
| 131 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(gaD/C) | |
| 132 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(czC/D) | |
| 133 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(pvC/D) | |
| 134 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(laD/C) | |
| 135 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(dlD/C) | |
| 136 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(gaD/C) | View |

*Figure 44: Generation of Flowsheet tab*

### 4.2.5 Ranking of Flowsheets Tab:

This tab provides access to for the user to interact, where the user can select from different flowsheet property models (as shown in the Figure 45) and rank the alternatives. The right pane in the window shows the available property models and the left pane of the window shows all the generated process alternatives along with the selected property value. Here the user has access to choose more than one property model and the tool will evaluate.



| Rank | Design-Alternative | Energy-Index | Carbon-Footprint | ProdRec:D | Prod |
|---|---|---|---|---|---|
| 185 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(dlC/AB) | 3.714217931413... | 21.385 | 0.97 | 0.98 |
| 184 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(flC/AB) | 3.702167415651... | 13.278 | 0.975 | 0.985 |
| 183 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(gaC/AB) | 3.702167415651... | 13.278 | 0.97 | 0.98 |
| 170 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(dlD/C) | | 15.678 | 0.975 | 0.985 |
| 165 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(dl | | | 0.975 | 0.98 |
| 160 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC | | | | 0.985 |
| 173 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(ga | | | | 0.98 |
| 168 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD | | | | 0.985 |
| 182 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(laD/CA | | | | 0.98 |
| 166 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(ga | | | 0.975 | 0.985 |
| 169 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(laD/C) | | 10.420 | 0.97 | 0.98 |
| 167 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(czC/D) | 2.392902408496... | 10.420 | 0.975 | 0.985 |
| 176 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(dlD/AB) | 2.391369241100... | 10.417 | 0.975 | |
| 179 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(pvC/DAB)(dlD/AB) | 2.391369241100... | 10.417 | 0.98 | |
| 164 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(laD/C) | 2.380851892734... | 5.197 | | |
| 162 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(czC/D) | 2.380851892734... | 5.197 | | |
| 171 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaD/CAB)(gaC/AB) | 2.380851892734... | 5.197 | | |
| 159 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(laD/C) | 2.380851892734... | 5.197 | 0.98 | |
| 163 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(pvC/D) | 2.380851892734... | 5.197 | 0.98 | |
| 174 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(gaD/AB) | 2.380851892734... | 5.197 | 0.975 | 0.985 |
| 175 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(flD/AB) | 2.380851892734... | 5.197 | 0.975 | 0.985 |
| 158 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(pvC/D) | 2.380851892734... | 5.197 | 0.98 | 0.985 |

● Energy consumption
○ Carbon Footprint
○ Product recovery

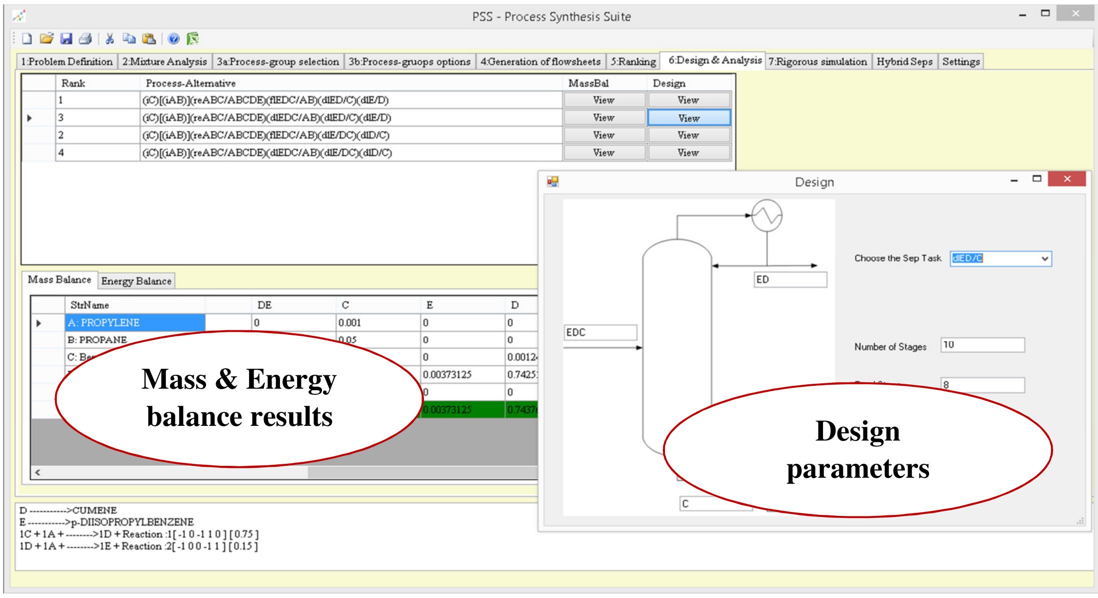
☐ Product stream: oAB
☐ Product stream: oC
☑ Product stream: oD
☑ Product stream: oE

```
D ----------->CUMENE
E ----------->p-DIISOPROPYLBENZENE
1C + 1A + -------->1D + Reaction :1[ -1 0 -1 1 0 ] [ 0.75 ]
1D + 1A + -------->1E + Reaction :2[ -1 0 0 -1 1 ] [ 0.15 ]
```

*Figure 45: Ranking of Flowsheets Tab in Process Synthesis Suite*

### 4.2.6 Design and Analysis Tab:

In this tab, the process-groups are replaced by simple mixers and/or splitters to evaluate mass and enthalpy balances across the unit operations. Stream summary of all the inlet and outlet streams, along with energy balance results, can be visualized by the user in this form. In this form the user has access to view the calculated design parameters, like number of stages and feed location of distillation columns, of the unit operations as shown in Figure 46.



| Rank | Process-Alternative | MassBal | Design |
|---|---|---|---|
| 1 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(dlE/D) | View | View |
| 3 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(dlE/D) | View | View |
| 2 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(dlD/C) | View | View |
| 4 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(dlD/C) | View | View |

| StrName | DE | C | E | D |
|---|---|---|---|---|
| A: PROPYLENE | 0 | 0.001 | 0 | 0 |
| B: PROPANE |  | 0.05 | 0 | 0 |
| C: Be |  |  | 0 | 0.0012 |
|  |  |  | 0.00373125 | 0.7425 |
|  |  |  | 0 | 0 |
|  |  |  | 0.00373125 | 0.7437 |

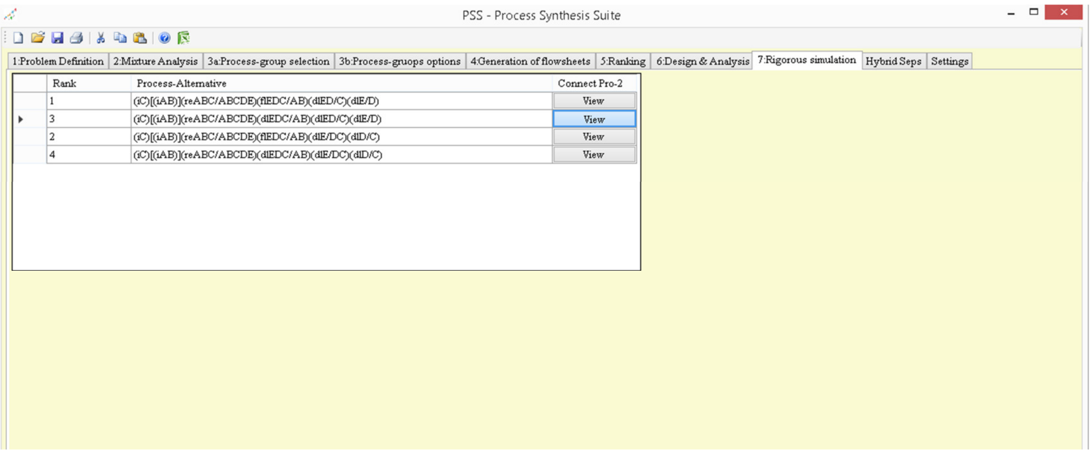
D ----------->CUMENE
E ----------->p-DIISOPROPYLBENZENE
1C + 1A + -------->1D + Reaction :1[ -1 0 -1 1 0 ] [ 0.75 ]
1D + 1A + -------->1E + Reaction :2[ -1 0 0 -1 1 ] [ 0.15 ]

Choose the Sep Task: dlED/C
Number of Stages: 10
8

*Figure 46: Design and Analysis Tab in Process Synthesis Suite*

### 4.2.7 Rigorous Simulation Tab:

The user can generate the detailed simulation file for the selected alternatives and can directly invoke commercial simulation tools, like ProII, from the software.



| Rank | Process-Alternative | Connect Pro-2 |
|---|---|---|
| 1 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(dlE/D) | View |
| 3 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(dlE/D) | View |
| 2 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(dlD/C) | View |
| 4 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(dlD/C) | View |

*Figure 47: Rigorous Simulation Tab in Process Synthesis Suite*

All the process-groups of the selected alternative are converted to simulator rigorous models and setup using process-group definitions and results from various steps of the method. The setting up of the rigorous simulation is explained in section 3.1.7. Figure 48 gives the screenshot of the ProII simulation file generated by the process synthesis tool.

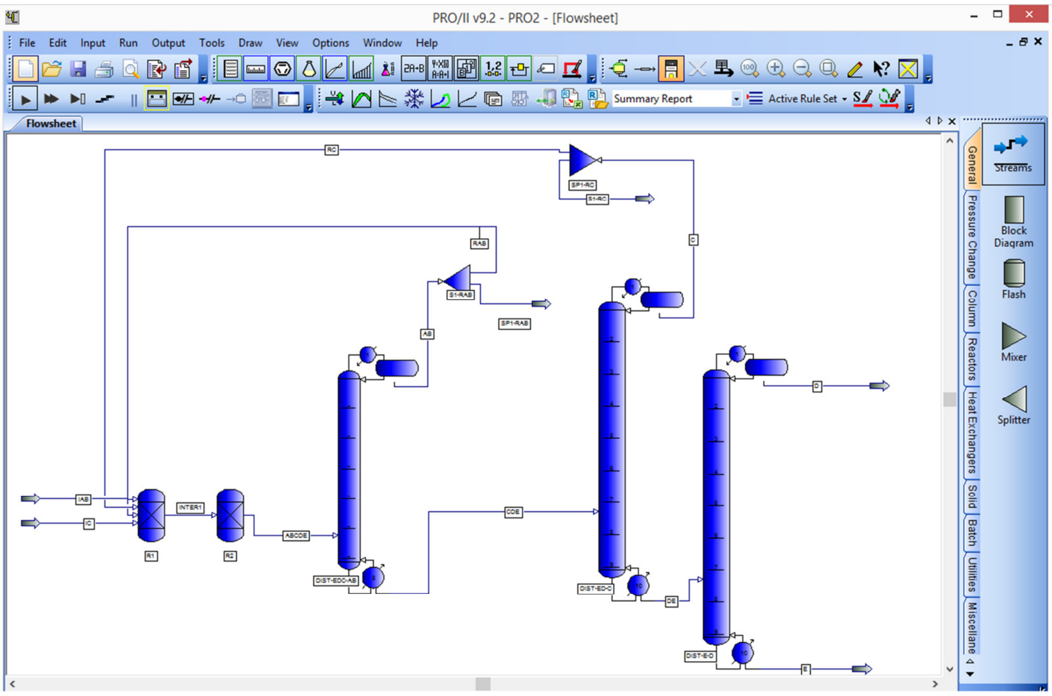


*Figure 48: Generated Pro-II file from Process Synthesis Suite*

# 5

# APPLICATION EXAMPLES

In this chapter the developed sustainable process synthesis-design and analysis method is illustrated through several industrial case studies. Each of the case studies focuses on a specific part of the method, like hybrid separations, in order to highlight the corresponding step of the method. The main focus for each case study is summarized below:

- In section 5.1, sustainable process synthesis-design and analysis method is applied to a case study involving the production of benzene from toluene. This case study has been selected to highlight the application of the method, with respect to the representation of a process flowsheet with process-groups, and for generating new as well as existing flowsheet alternatives for producing benzene from toluene and hydrogen. Also, since a number of alternative designs for this process are reported, there is a bench-mark for the new results. In this case study the simultaneous process optimization and heat integration step of the method is also highlighted.

- In section 5.2, the method is applied to a bioprocess involving production of bioethanol from lignocellulosic biomass. In this case study, apart from generating new process designs, the focus is on generating alternatives based on the solvent-based process-groups, for the separation of water-ethanol azeotrope. In this case study the solvent design problem is also highlighted.

- In section 5.3, the hybrid separations step of the method is highlighted in the case study involving separation of alkane isomers. In this case study, the synthesis-design of hybrid distillation-membrane is applied to replace distillation columns in the top ranked alternative to further improve the process.

- In section 5.4, other application examples of industrial importance where the method was able to generate feasible alternatives are briefly explained.

## 5.1 HYDRODEALKYLATION OF TOLUENE

### 5.1.1 Step 1 Synthesis Problem Definition:

The synthesis problem definition is to produce benzene from toluene and hydrogen. This toluene hydrodealkylation is highly exothermic and typical operating conditions are from 700 K to 850 K, and around 40 bar. The structural definition of the synthesis problem as shown in Figure 49 is as follows: 2 inlets of toluene and hydrogen, 1 outlet of benzene. As hydrogen is only available with methane impurities, the inlet definition for hydrogen stream also includes methane (dilute component).

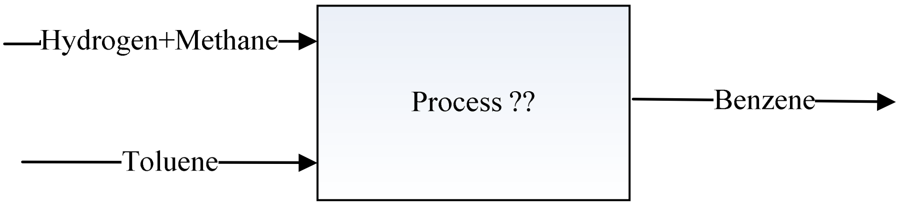


*Figure 49: Structural definition of the synthesis problem*

Stream composition, temperature and pressure information for both the inlet streams is given by Table 15. The design constraint for this synthesis problem is that the minimum product purity (benzene) should be 99.8 mol %.

*Table 15: Inlet stream conditions for the given synthesis problem*

| | **Inlet 1** | **Inlet 2** |
|---|---|---|
| (A) Hydrogen, kmol/hr | 0 | 178.48 |
| (B) Methane, kmol/hr | 0 | 5.52 |
| (C) Benzene, kmol/hr | 0 | 0 |
| (D) Toluene , kmol/hr | 136 | 0 |
| (E) Biphenyl, kmol/hr | 0 | 0 |
| Temperature, k | 298 | 298 |
| Pressure, atm | 40 | 40 |

The flowsheet property specification or the performance criterion for this problem is minimum energy consumption per kilogram of product produced.

## 5.1.2 Step 2 Problem Analysis:

In this step all the necessary information required to solve the synthesis problem is generated. This is carried out in 3 tasks: i) reaction analysis, ii) mixture analysis and iii) feasible separation task identification.

### 5.1.2.1 Reaction Analysis

The reaction analysis has confirmed the possibility to produce benzene by toluene hydrodealkylation (see equation 5.1). The search in the reaction database also confirmed the secondary reaction of producing biphenyl from benzene (see equation 5.2). The reaction database provides conversion rates for the reactions. As biphenyl is found to have financial value, the structural problem definition of the synthesis problem is refined to include a second outlet for biphenyl recovery as shown in Figure 50.

$$\text{Hydrogen+Toluene} \rightleftarrows \text{Methane+Benzene} \tag{5.1}$$

$$\text{2Benzene} \rightleftarrows \text{Hydrogen+Biphenyl} \tag{5.2}$$

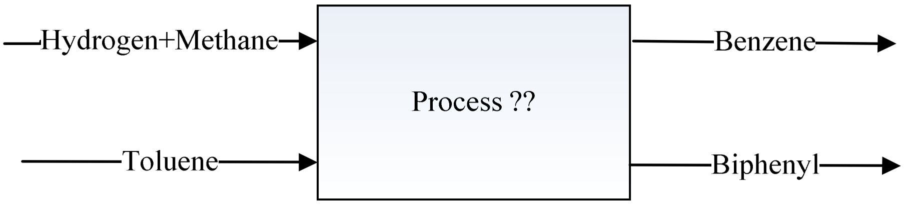


*Figure 50: Updated structural definition of the synthesis problem*

### 5.1.2.2 Mixture Analysis

The analysis of the pure component properties in the process design problem is performed after retrieving the 22 pure component properties of the chemical components from the compound property database. The pure component properties of all the compounds identified in the synthesis problem are listed in the Table 16.

The five compounds in the system form 10 binary pairs. No binary azeotropes are detected in the azeotropic analysis carried out using Azeopro. The binary ratio matrix of pure component properties for all binary pairs is calculated and selected properties are shown in the Table 17.

*Table 16: Pure component properties. Refer to Table 4 for annotations*

| **Property** | **Toluene** | **Hydrogen** | **Biphenyl** | **Methane** | **Benzene** |
|---|---|---|---|---|---|
| $M_w$ (g/mol) | 92 | 2 | 154 | 16 | 78 |
| $\omega$ | 0.26 | -0.22 | 0.37 | 0.01 | 0.21 |
| $T_c$ (K) | 592 | 33 | 789 | 191 | 562 |
| $P_c$ (bar) | 41 | 13 | 38 | 45 | 48 |
| $Z_c$ | 0.26 | 0.31 | 0.30 | 0.29 | 0.27 |
| $V_c$ ($m^3$/kmol) | 0.32 | 0.06 | 0.50 | 0.10 | 0.26 |
| $T_b$ (K) | 384 | 20 | 528 | 112 | 353 |
| $d_m \times 1 \cdot 10^{-30}$ $(C \cdot m)$ | 0.36 | 0 | 0 | 0 | 0 |
| $r_g$ (Å) | 3.47 | 0.37 | 4.83 | 1.12 | 3.00 |
| $T_m$ (K) | 178.2 | 14 | 342 | 91 | 279 |
| $T_{tp}$ (K) | 178 | 14 | 342 | 91 | 279 |
| $P_{tp}$ (Pa) | 4.2E-07 | 7.1E-02 | 9.3E-04 | 1.2E-01 | 4.7E-02 |
| $M_v$ ($m^3$/kmol) | 1.1E-01 | 2.9E-02 | 1.6E-01 | 3.8E-02 | 8.9E-02 |
| $H_f$ (kJ/kmol) | 50170 | 0 | 182420 | -74520 | 82880 |
| $G_f$ (kJ/kmol) | 122200 | 0 | 280230 | -50490 | 129600 |
| $S_{IG}$ $(kJ/kmol \cdot K)$ | 321 | 131 | 394 | 186 | 269 |
| $H_{fus}$ (kJ/kmol) | 6636 | 117 | 18580 | 941 | 9866 |
| $H_{comb}$ (kJ/kmol) | -3734000 | -241820 | -6031700 | -802620 | -3136000 |
| $\delta$ ($\sqrt{}$ kJ/$m^3$) | 18 | 7 | 19 | 12 | 19 |
| $V_{vw}$ ($m^3$/kmol) | 6.0E-02 | 6.3E-03 | 9.2E-02 | 1.7E-02 | 4.8E-02 |
| $A_{vw}$ ($m^2$/kmol) | 7.42E+08 | 1.43E+08 | 10.70E+08 | 2.88E+08 | 6.00E+08 |
| $P_{nvap}$ (Pa) | 0.38E+04 | Very high | Very low | 6180.23E+04 | 1.26E+04 |

*Table 17: Binary ratio matrix for a select set of properties. Tb - normal boiling point, RG - radius of gyration, Tm - normal melting point, Mv - molar volume, SolPar - solubility parameter, Vvw - Van der Waals volume, Pnvap - vapor pressure*

| **Binary pair** | | **Tb** | **RG** | **Tm** | **Mv** | **SolPar** | **Vvw** | **Pnvap** |
|---|---|---|---|---|---|---|---|---|
| Toluene | Hydrogen | 3.13 | 4.93 | 18.82 | 12.78 | 2.46 | 56.67 | 1.8E+17 |
| | Biphenyl | 2.93 | 7.83 | 25.90 | 24.54 | 3.02 | 158.67 | 1.0E+03 |
| | Methane | 1.19 | 5.09 | 4.73 | 3.77 | 2.11 | 19.74 | 1.6E+04 |
| | Benzene | 1.06 | 2.63 | 3.16 | 3.07 | 1.45 | 10.48 | 3.3E+00 |
| Hydrogen | Biphenyl | 25.90 | 13.03 | 24.54 | 5.44 | 2.90 | 14.51 | 1.9E+20 |
| | Methane | 5.48 | 3.01 | 6.50 | 1.33 | 1.74 | 2.70 | 1.1E+13 |
| | Benzene | 17.32 | 8.10 | 19.98 | 3.13 | 2.82 | 7.66 | 5.4E+16 |
| Biphenyl | Methane | 4.73 | 4.32 | 3.78 | 4.09 | 1.66 | 5.38 | 1.7E+07 |
| | Benzene | 1.50 | 1.61 | 1.23 | 1.74 | 1.03 | 1.89 | 3.4E+03 |
| Methane | Benzene | 3.16 | 2.69 | 3.07 | 2.36 | 1.61 | 2.84 | 4.9E+03 |

#### 5.1.2.3 Feasible Separation Task Analysis

Feasible process operation techniques to separate each of the binary pairs are identified using Jaksland et al. (Jaksland, Gani, and Lien 1995) physical insights based method. Table 18 gives information on the feasible separation techniques identified for each of the binary pairs present in the synthesis problem.

### 5.1.3 Step 3 Process-groups Selection:

From the previous step, problem analysis, all the needed information is available to represent the process flowsheet with process groups.

- Inlet and Outlet process-groups: From the problem definition step, two inlet process-groups representing pure toluene stream and hydrogen with methane impurity are identified. Two outlet process-groups representing benzene and biphenyl products streams are also selected for this synthesis problem.
- Reactor process-group: The hydrodealkylation reaction of toluene in presence of hydrogen to produce benzene has been identified. The reaction is performed in a single reactor. From the problem analysis, the reaction, together with the conversion, is known. The reactor can be represented with a fixed conversion based reactor process group.

*Table 18: Separation techniques identified for each binary pair in the synthesis problem*

| **Binary pair** | **Separation Tasks Identified** |
|---|---|
| Hydrogen - Methane | Gas adsorption, Flash, Gas Separation Membranes, Partial Condensation |
| Hydrogen - Benzene | Absorption, Gas Adsorption, Flash, Partial Condensation |
| Hydrogen - Toluene | Absorption, Gas Adsorption, Flash, Partial Condensation |
| Hydrogen - Biphenyl | Absorption, Flash, Partial Condensation |
| Methane - Benzene | Gas Adsorption, Flash, Partial Condensation, Stripping |
| Methane - Toluene | Gas adsorption, Flash, Partial Condensation, Stripping |
| Methane - Biphenyl | Flash, Partial Condensation |
| Benzene - Toluene | Gas adsorption, Crystallization, Distillation, Extractive Distillation, Liquid Membrane Separation, Pervaporation, Liquid Adsorption |
| Benzene - Biphenyl | Flash, Liquid Membrane Separation, Pervaporation, Liquid Adsorption |
| Toluene - Biphenyl | Crystallization, Flash, Liquid Membrane Separation, Pervaporation , Liquid Adsorption |

- Separation process-groups: From the separation task identification analysis carried out in step 5.1.2.3, all feasible separation techniques, as applicable for the synthesis problem, are identified as shown in Table 18. Using this information, process-groups representing the separation techniques are retrieved from the process-groups database. These selected process-groups are initialized with all possible combinations of chemical species. Table 19 shows all the initialized process groups for production of Benzene from Toluene and Hydrogen. Since, in the problem definition step, methane is considered as impurity (dilute component), there is no separation task identified for separating methane and hydrogen. If methane is not considered a dilute impurity, then one more process group (gm A/B) is added to the list to separate hydrogen and methane and recycle back hydrogen to reactor.

*Table 19: Initialized process groups for the synthesis problem.*

| **Operation type** | **Gas membrane separation** | **Molecular-sieve separation** | **Distillation** | **Crystallization** | **Liquid membrane separation** |
|---|---|---|---|---|---|
| **Process groups** | gmE/DCAB | msE/DCAB | dlABCD/E | crE/C | lmE/C |
| | gmD/CAB | msD/CAB | dlABC/D | crE/D | lmD/C |
| | gmC/AB | msC/AB | dlAB/C | crE/CD | lmED/C |
| | gmED/CAB | msE/D | dlABC/DE | crEC/D | lmE/D |
| | gmE/D | msED/C | dlAB/CDE | crC/D | lmE/DC |
| | gmDC/AB | msDC/AB | dlC/D | | |
| | gmED/C | msED/CAB | dlAB/CD | **Inlet/Outlet** | **Reactor** |
| | gmD/C | msD/C | dlC/DE | iAB | rABD/ABCDE |
| | gmE/C | msE/DC | dlD/E | iD | |
| | gmEDC/AB | msE/C | dlC/E | oC | |
| | gmE/DC | msEDC/AB | | oE | |

## 5.1.4 Step 4 Generation of Flowsheets:

In this step, firstly, the superstructure of all feasible alternatives is generated and corresponding SFILES are generated for all the identified process alternatives.

### 5.1.4.1 Superstructure generation

The flowsheet generation method, as explained in section 2.2.2.2, is used to generate a superstructure of all possible flowsheets from the 47 initialized process-groups. Around 74,000 flowsheet combinations are available for the given synthesis problem; but, after applying the combinatorial algorithm, where structurally infeasible alternatives are discarded, the number of process alternatives available was reduced to 272. These structurally feasible alternatives are further reduced by using logical rules. The statistics of the method are given in Table 20.

*Table 20: Computational statistics for the synthesis problem.*

| **Statistics** | |
|---|---|
| Number of process groups | 47 |
| Flow sheet combinations | 74,046 |
| Structurally feasible combinations | 272 |
| Final process alternatives | 32 |

Figure 51 represents all 272 structurally feasible flowsheets generated for production of benzene from toluene and hydrogen. The 32 process alternatives identified by the reduction algorithm are represented by blue arrows. The process alternatives will be 64 if we consider both the case where methane is considered as dilute impurity and the case where methane is a non-dilute component.

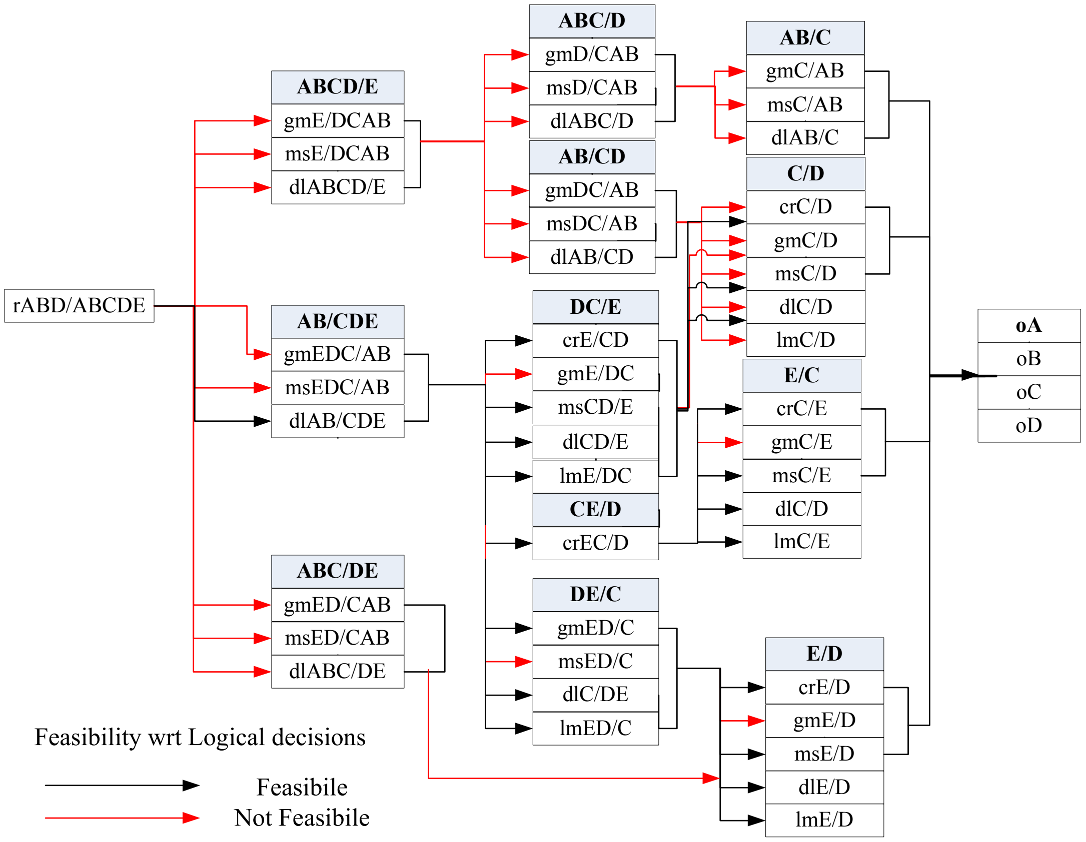


*Figure 51: Superstructure of alternatives for HDA synthesis problem*

### 5.1.4.2 Generation of SFILES

All the identified process alternatives are converted into SFILES, which store the structural information of the alternatives. Table 21 gives selected alternatives for the given problem. For the list all alternatives generated refer to Table D1 (Appendix D).

*Table 21: SFILES of generated process alternatives.*

| Sno | SFILES |
|---|---|
| 1 | (iAB)(rAD/ABCDE)<1<2[(<iD)](dlAB/CDE)[(oAB)1](dlC/DE)[(oC)](crE/D)[(oD)2](oE) |
| 2 | (iAB)(rAD/ABCDE)<1<2[(<iD)](dlAB/CDE)[(oAB)1](dlC/DE)[(oC)](D/E)[(oD)2](oE) |
| 3 | (iAB)(rAD/ABCDE)<1<2[(<iD)](dlAB/CDE)[(oAB)1](dlC/DE)[(oC)](msE/D)[(oD)2](oE) |
| 4 | (iAB)(rAD/ABCDE)<1<2[(<iD)](dlAB/CDE)[(oAB)1](lmED/C)[(oC)](crE/D)[(oD)2](oE) |
| 5 | (iAB)(rAD/ABCDE)<1<2[(<iD)](dlAB/CDE)[(oAB)1](dlC/DE)[(oC)](lmE/D)[(oD)2](oE) |

Some of the designs generated using this method can be found in literature. For example, design 2 is proposed by Douglas (1985) and design 34 is proposed by Bouton and Luyben (2008). Also, 2 more designs resembling alternative 34 with minor modifications are proposed Konda et al. (2006).

### 5.1.5 Step 5 Ranking of Flowsheets:

Table 22 provides the top five process alternatives ranked with respect to energy consumption of the process. Energy consumption for the alternatives is calculated using the energy index flowsheet property model, as described in section 2.2.2.4. In addition to using the energy index, the minimum purity of both product streams is also estimated using the flowsheet property models. The first two designs, reported in Table 22, have the same energy index. This is explained by the fact that the energy index Ex is only calculated for the distillation process groups, the other process groups do not contribute to the energy index (contribution equals to 0.0).

*Table 22: Top ranked process alternatives for the synthesis problem.*

| **Design No** | **Energy Index** | **Benzene Purity** (mol %) | **Biphenyl Purity** (mol %) | **Carbon Footprint** ($CO_2$ Eq) |
|---|---|---|---|---|
| 1 | 0.0539 | 99.8 | 99.9 | 0.118 |
| 2 | 0.0539 | 99.8 | 99.0 | 0.118 |
| 3 | 0.0641 | 99.8 | 99.5 | 0.140 |
| 4 | 0.0670 | 99.8 | 99.9 | 0.146 |
| 5 | 0.0772 | 99.8 | 99.5 | 0.169 |

### 5.1.6 Step 6 Process Design:

The first task is to resolve the mass balance of the top ranked flowsheets in order to calculate the design parameters and to conduct post-analysis. Using simple models, the mass balance is resolved and the overall benzene production of each alternative is calculated. Along with mass resolution, as the composition across all process groups is now known, it is possible to estimate the energy required by each unit operation of the flowsheet; the corresponding energy requirements are shown in Table 23.

*Table 23: Mass and Energy balance results for Top ranked processes*

| **Design No** | **Energy** (MkJ/hr) | **Benzene** (kmol/hr) |
|---|---|---|
| 1 | 27.87 | 127.8 |
| 2 | 27.71 | 127.5 |
| 3 | 28.57 | 127.3 |
| 4 | 28.58 | 127.8 |
| 5 | 29.03 | 127.5 |

Design parameters of the unit operations present in the process alternatives are calculated using the reverse simulation method as explained in step 2.2.5. Table 24 gives the design data for the distillation columns present in the second process alternative (design no 2).

*Table 24: Design of distillation column using driving force method.*

| **Distillation column design (driving force method)** | **Stabilizer** | **Benzene column** | **Toluene column** |
|---|---|---|---|
| Given a NC component process group | 5 | 3 | 2 |
| Order the components with respect to relative volatility | AB/CDE | C/DE | D/E |
| Driving force between the key components FDimax ,Di | >0.75 | 0.22 , 0.4 | 0.6 , 0.25 |
| Recovery of light key | 0.999 | 0.995 | 0.995 |
| Recovery of heavy key | 0.999 | 0.995 | 0.995 |
| $N_{ideal * 1.5}$ | 5 | 31 | 15 |
| $N_f$ Feed location | 2 | 19 | 12 |

### 5.1.7 Step 7 Rigorous Simulation:

The process alternatives 1 and 2 are selected for rigorous simulation by means of a commercial process simulator (PROII). The first process alternative is a novel processing route for production of benzene through toluene hydrodealkylation, whereas the second alternative obtained through this method is similar to the processing route proposed by Douglas (1985).

Process alternative 1:

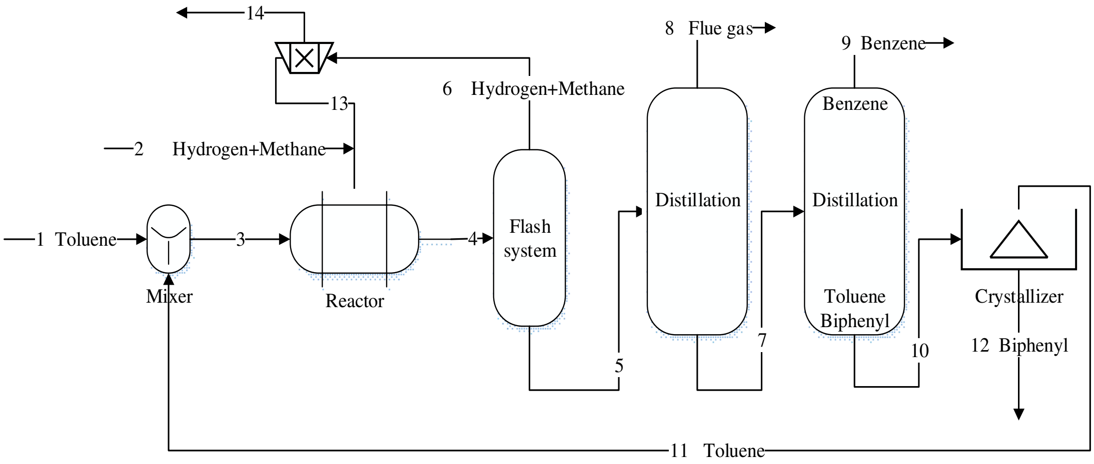


*Figure 52: Process flowsheet for generated alternative 1*

In the first alternative, the benzene production from toluene hydrodealkyaltion resembles the flowsheet proposed by Douglas (1985), except the last distillation column is replaced by a crystallization unit to separate biphenyl. Using crystallization to recover biphenyl from HDA process has been reported and patented by Eugene (1966).

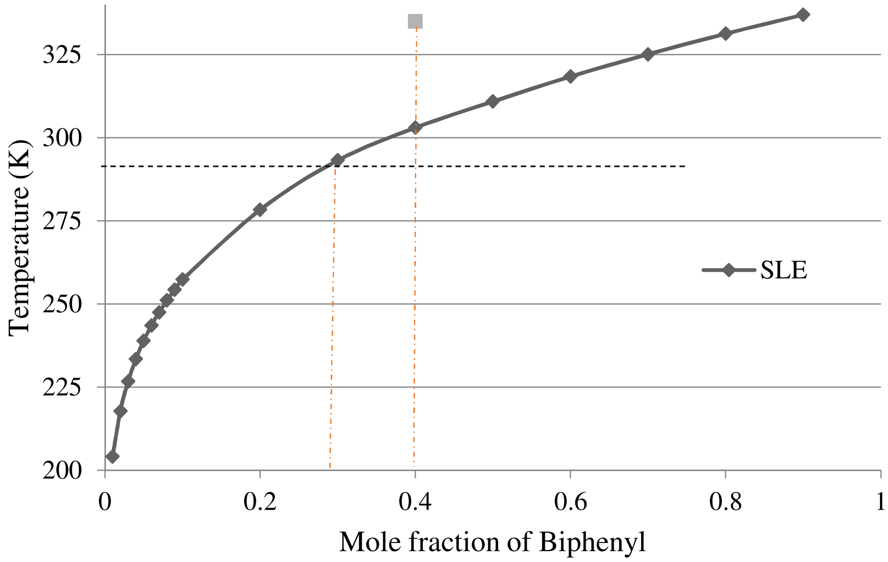


*Figure 53: Solid Liquid Equilibrium curve for Toluene and Biphenyl*

Solid liquid equilibrium simulation data for Toluene and Biphenyl is shown in Fig 53, which is generated using ICAS (R Gani et al. 1997; R Gani 2002) and shows the possible recovery of biphenyl. This information is used in the process simulator to determine the recovery of Biphenyl. The mass balance results obtained from rigorous simulations are given in Table 25.

*Table 25: Mass balance results for generated alternative 1*

| **Stream (Summary)** | **S2** | **S1** | **S6** | **S9 Benzene** | **S11** | **S12 Biphenyl** |
|---|---|---|---|---|---|---|
| Phase | Vapor | Liquid | Vapor | Liquid | Liquid | Solid |
| Total Molar Rate kg-mol / hr | 299.8 | 135.9 | 1443.3 | 126.6 | 66.2 | 3.5 |
| Temperatur, Ke | 298.0 | 298.0 | 305.0 | 353.3 | 295.0 | 295.0 |
| Pressure, Atm | 40.0 | 40.0 | 40.0 | 1.0 | 1.0 | 1.0 |
| Component Rates, kg-mol / hr | | | | | | |
| H2 | 290.82 | 0.00 | 767.08 | 0.00 | 0.00 | 0.00 |
| METHANE | 8.99 | 0.00 | 672.17 | 0.00 | 0.00 | 0.00 |
| TOLUENE | 0.00 | 135.90 | 0.39 | 0.22 | 44.57 | 0.00 |
| BENZENE | 0.00 | 0.00 | 3.70 | 126.37 | 0.64 | 0.00 |
| BIPHENYL | 0.00 | 0.00 | 0.00 | 0.00 | 21.03 | 3.48 |

Process Alternative 2:

This processing route is same as the one proposed by Douglas (1985) for production of benzene from toluene. In this particular alternative, the downstream separation consists of 3 distillation columns to separate the unreacted raw materials and the products. The stream summary of this alternative obtained from rigorous simulation is given by the Table 26.

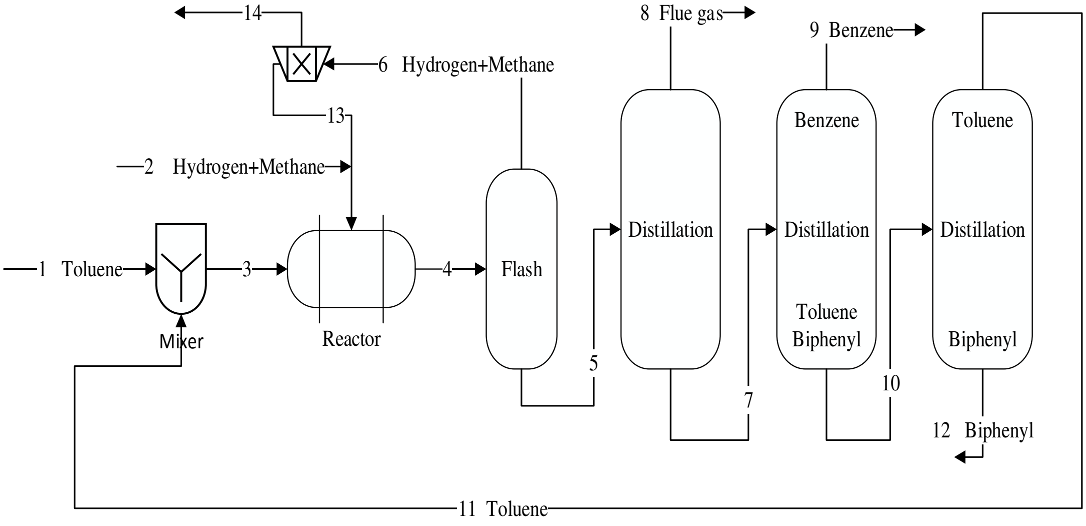


*Figure 54: Process flowsheet for generated alternative 2*

*Table 26: Mass balance results for benzene production by process alternative 2*

| **Stream (Summary)** | **S2** | **S1** | **S6** | **S9 Benzene** | **S11** | **S12 Biphenyl** |
|---|---|---|---|---|---|---|
| Phase | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| Total Molar Rate kg-mol / hr | 299.0 | 135.9 | 1448.2 | 126.6 | 45.1 | 3.5 |
| Temperatur, Ke | 298.0 | 298.0 | 305.0 | 353.3 | 383.7 | 524.8 |
| Pressure, Atm | 40.0 | 40.0 | 40.0 | 1.0 | 1.0 | 1.0 |
| Component Rates, kg-mol / hr | | | | | | |
| H2 | 290.00 | 0.00 | 766.23 | 0.00 | 0.00 | 0.00 |
| METHANE | 8.97 | 0.00 | 677.39 | 0.00 | 0.00 | 0.00 |
| TOLUENE | 0.00 | 135.90 | 0.44 | 0.22 | 44.46 | 0.02 |
| BENZENE | 0.00 | 0.00 | 4.14 | 126.41 | 0.64 | 0.00 |
| BIPHENYL | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 3.49 |

Comparing alternative 1 and 2:

The first process alternative obtained from the method has slightly improved heating energy efficiency with respect to the alternative proposed in the literature. But due to the fact that biphenyl is removed using crystallization in the last separation step the cooling utilities ( from Table 27) increased. It is also observed that the compressor duty more in alternative 1 as some of the biphenyl is recycled along with toluene.

*Table 27: Comparison of energy requirements and production rates for the two process alternatives*

| | **Heating** M KJ/hr | **Cooling** M KJ/hr | **Benzene** kg-mol/hr | **Biphenyl** kg-mol/hr |
|---|---|---|---|---|
| Process alternative 1 | 34.57 | -43.67 | 126.37 | 3.48 |
| Process alternative 2 | 34.78 | -39.98 | 126.41 | 3.49 |

**Economic Analysis:** Economic analysis is performed on the process alternative 1 using ECON. Figure 55 shows the distribution of utility cost between the unit operations present in the process flowsheet. From this analysis, it is clear that heat exchangers (HE1, HE2, HE3, HE4) consume more than 65 % of the total utilities of the process.

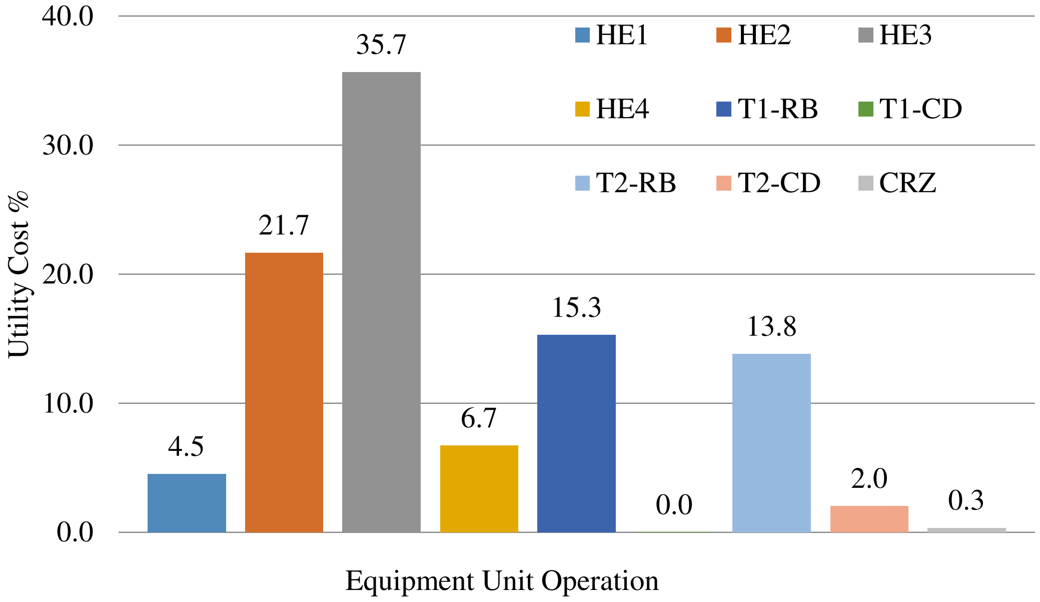


*Figure 55: Economic analysis of process alternative -1.*

**Sustainability Analysis:** The three most critical paths in the entire process flowsheet which has highest potential for improvement have been identified and are given by Table 28. OP2 and OP7 follow the raw materials hydrogen and methane and have a negative value for value addition, which means the raw materials in this path are losing value because of the presence of the purge stream. For CP9, the high EWC indicator shows that toluene is recycled in high rates, which is increasing the heat duties in this path.

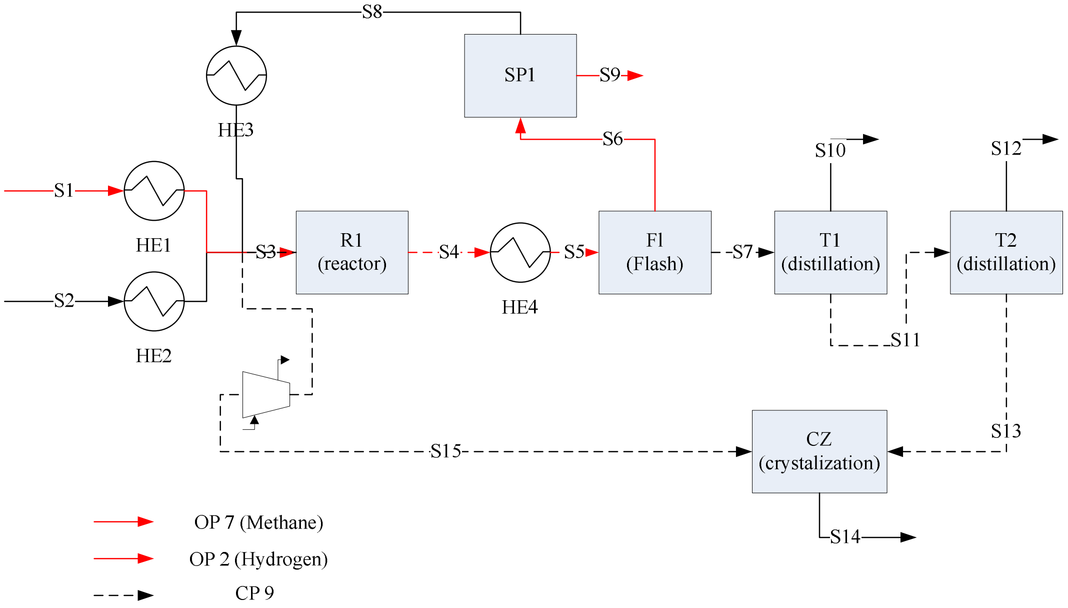


*Figure 56: Selected base case design for production benzene. The open and closed paths (OP, CP) are also highlighted.*

*Table 28: Sustainability analysis of process alternative -1*

| **Path** | **Component** | **Flow-rate** (kg/h) | **MVA** ($10^3$\$/yr) | **EWC** ($10^3$\$/yr) | **TVA** ($10^3$\$/yr) |
|---|---|---|---|---|---|
| OP 2 | H2 | 283.2 | -3258.9 | 34.04 | -3293.02 |
| OP 7 | METHANE | 2005.5 | -9843.8 | 8.8 | -9852.6 |
| CP 9 | TOLUENE | 4094.3 | - | 662.7 | - |

**Life Cycle Analysis:** Environmental assessment of the process is carried out using LCSoft. Figure 57 gives the carbon footprint of different equipment present in the process. From the analysis, it is clear that major source of carbon dioxide is from the four heat exchangers (HE1, HE2, HE3, HE4). Table 29 gives the estimated environmental impact factors for the selected base case.

*Table 29: Environmental assessment of process alternative -1*

| | **Environmental Impact Factors** | | | |
|---|---|---|---|---|
| **Process Alternative** | HTPI | HTPE | ATP | GWP |
| **Base case** | 51.05 | 47.78 | 59.2 | 7.9 |

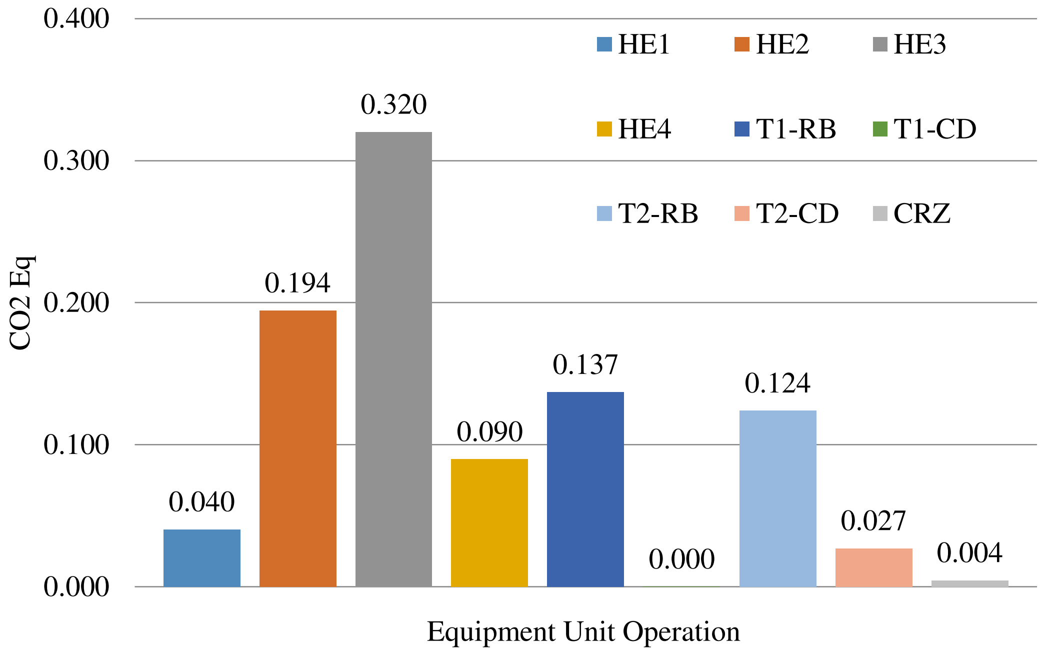


*Figure 57: Carbon Footprint of variuos equipment in process alternative -1*

Based on the analysis, using Table 7 and 8 the following design targets are identified:

- Reduce raw material loss
- Reduce energy consumption
- Reduce utility cost
- Improvements in LCA/Sustainability indicators
- Product purity (kept as the base case)
- Production target (kept as the base case)
- Reduce operational cost

### 5.1.8 Step 8 Innovative Designs:

In this case study the simultaneous optimization and heat integration strategy is used to target the identified process hotspots. In this case study the process is optimized to maximize the operational profit and the heat integration targeting heat exchangers (HE1, HE2, HE3, HE4) which were identified from economic and life cycle analysis.

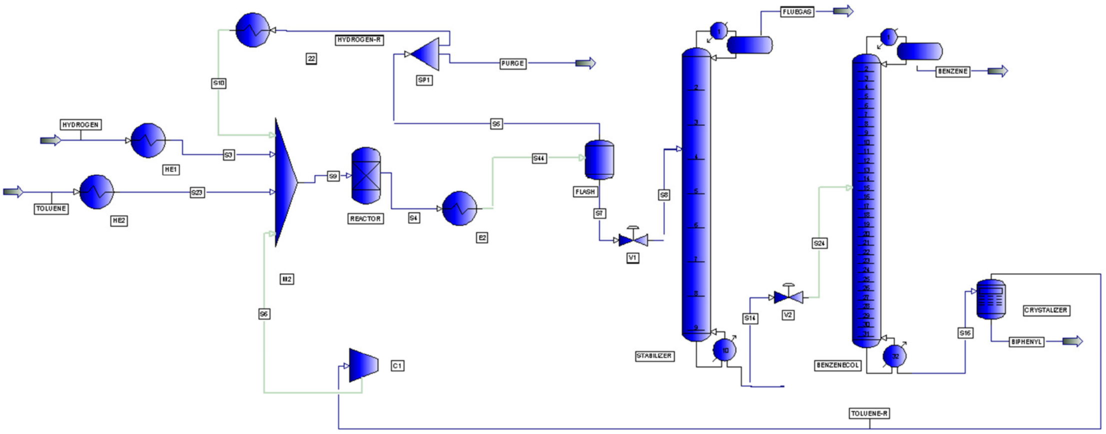


*Figure 58: Base case for hydrodealkylation of toluene (Process alternative 1)*

The objective function defined for this case study is to maximize operational profit. Operational profit is given by the Equation 5.3.

Profit = Total revenue – Total operating cost (5.3)

Total revenue = Products sale (benzene, biphenyl) * cost + Heating value (hydrogen, methane) *cost

Total operating cost = Heat loads (HE1, HE2, HE3, HE4, reboiler-stabilizer column, condenser-stabilizer column, reboiler-benzene column, condenser -benzene column, crystallizer) * cost

Along with the profit optimization, a better design is also investigated by including purge ratio as a constraint to the optimization problem in order to reduce the hot spot concerning sustainability and life cycle analysis.

*s.t.* 0.75 < recycle stream flow rate / purge stream flow rate < 0.85 (5.4)

*Table 30: Cost data for HDA problem*

| **Feedstock or product** | | **USD /Kg-mol** |
|---|---|---|
| Hydrogen feed | 95 % $H_2$ | 2.5 |
| Toluene feed | 100% | 14 |
| Benzene product | >99% | 19.9 |
| Biphenyl product | >99% | 11.84 |
| Hydrogen purge | (heating value) | 1.08 |
| Methane purge | (heating value) | 3.37 |
| **Utilities** | | **USD /unit** |
| Electricity | | 0.04 kW |
| Heating (steam) | | 8.0 MkJ |
| Cooling (water) | | 0.7 MkJ |

Table 30 gives the cost data used for this case study, while Table 31 gives the input data for heat integration module.

*Table 31: Input data for heat integration module*

| Value | Heat Integration module variable |
|---|---|
| 10 | HRAT |
| 400 | hot utility temperature C |
| 15 | cold utility temperature C |
| 1 | Number of hot streams |
| 3 | Number of cold streams |
| 1 | Number of hot utilities |
| 1 | Number of cold utilities |

Table 32 gives the comparison of various parameters for the base case and the optimized case. The profit has tripled for the optimized case when compared to the base case. This is mainly due to substantial reduction in heating and cooling utility requirements. Since the purge stream ratio is also optimized to maximize the profit, the waste generation also reduced which can be seen in reduction of various environmental properties. Figure 59 gives the final optimized flowsheet for production of benzene from toluene and hydrogen.

*Table 32: Improvements relative base case design*

| | Base case | Optimized Case | % Improvement |
|---|---|---|---|
| Objective function (USD/hr) | 152.55 | 456.60 | 199.3% |
| Purge ratio | 0.8 | 0.82 | 2.9% |
| Total Heating Utilities MkJ/hr | 34.57 | 11.35 | 67.2% |
| Total Cooling Utilities MkJ/hr | 43.67 | 28.42 | 34.9% |
| **Environmental parameters** | | | |
| HTPI | 51.05 | 43.90 | 14.0% |
| HTPE | 47.78 | 40.37 | 15.5% |
| ATP | 59.2 | 59.01 | 0.3% |
| GWP | 7.9 | 7.80 | 1.3% |

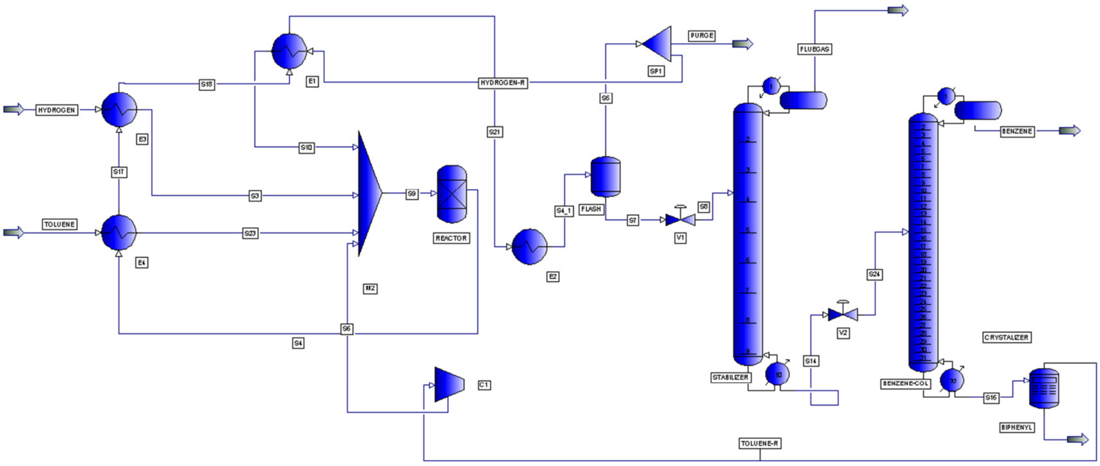


*Figure 59: Optimized design for hydrodealkylation of toluene*

## 5.2 BIOETHANOL PRODUCTION

### 5.2.1 Step 1 Synthesis Problem Definition:

The synthesis problem definition is to produce ethanol from lignocellulosic material. In this case study the focus is on generating novel solutions for downstream separation. The feedstock chosen for this case study is hard chips. The composition of the feedstock is given in the Table 33, taken from Wooley et al. (1999). The structural definition of the synthesis problem is as follows: 2 inlets of cellulose and enzymes, 2 outlets for ethanol and waste streams as shown in Figure 60.

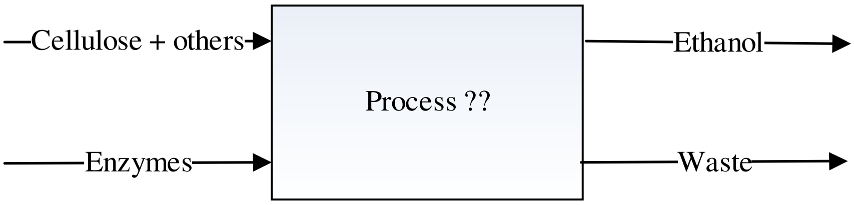


*Figure 60: Structural definition of the synthesis problem*

The design constraint for this synthesis problem is that the minimum product purity (ethanol) should be 99.5 mol %. The flowsheet property specification or the performance criteria for this problem minimum energy consumption per kg of product produced.

*Table 33: Feedstock composition*

| Compound | Dry weight % |
|---|---|
| Cellulose | 42.67 |
| Hemicellulose | 19.05 |
| Arabinan | 0.79 |
| Mannan | 3.93 |
| Galactan | 0.24 |
| Acetate | 4.64 |
| Lignin | 27.68 |
| Moisture | 47.9 |

### 5.2.2 Step 2 Problem Analysis:

In this step all the necessary information required to solve the synthesis problem is generated. This is carried out in 3 tasks: i) reaction analysis, ii) mixture analysis and iii) feasible separation task identification.

#### 5.2.2.1 Reaction Analysis

The reaction analysis has confirmed the possibility to produce ethanol from the given feed stock. The reactions (Wooley et al. 1999) along with conversions involved in scarification and fermentation are given below.

Scarification reactions:

$$C_6H_{10}O_5 + (0.5)H_2O \rightarrow (0.5)C_{12}H_{22}O_{11} \qquad \text{- Cellulose 0.012} \qquad (5.5)$$

$$C_6H_{10}O_5 + H_2O \rightarrow C_6H_{12}O_6 \qquad \text{- Cellulose 0.800} \qquad (5.6)$$

$$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \qquad \text{- Cellobiose 1.000} \qquad (5.7)$$

$$C_6H_{10}O_5 + (0.5)H_2O \rightarrow (0.5)C_{12}H_{22}O_{11} \qquad \text{- Cellulose 0.012} \qquad (5.8)$$

Fermentation reactions:

$$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \qquad \text{- Glucose 0.920} \qquad (5.9)$$

$$C_6H_{12}O_6 + 1.2NH_3 \rightarrow 6CH_{1.8}O_{0.5}N_{0.2} + 2.4H_2O + 0.3O_2 \qquad \text{- Glucose 0.027} \qquad (5.10)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow C_3H_8O_3 + O_2 \qquad \text{- Glucose 0.002} \qquad (5.11)$$

$$C_6H_{12}O_6 + 2CO_2 \rightarrow 2HOOCCH_2CH_2COOH + O_2 \qquad \text{- Glucose 0.008} \qquad (5.12)$$

$$C_6H_{12}O_6 \rightarrow 3CH_3COOH \qquad \text{- Glucose 0.022} \qquad (5.13)$$

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH \quad \text{- Glucose } 0.013 \tag{5.14}$$

$$3C_5H_{10}O_5 \rightarrow 5CH_3CH_2OH + 5CO_2 \quad \text{- Xylose } 0.850 \tag{5.15}$$

$$C_5H_{10}O_5 + NH_3 \rightarrow 5CH_{1.8}C_{0.5}N_{0.2} + 2H_2O + 0.25O_2 \quad \text{- Xylose } 0.029 \tag{5.16}$$

$$3C_5H_{10}O_5 + 5H_2O \rightarrow 5C_3H_8O_3 + 2.5O_2 \quad \text{- Xylose } 0.002 \tag{5.17}$$

$$C_5H_{10}O_5 + H_2O \rightarrow C_5H_{12}O_5 + 0.5O_2 \quad \text{- Xylose } 0.006 \tag{5.18}$$

$$3C_5H_{10}O_5 + 5CO_2 \rightarrow 5HOOCCH_2CH_2COOH + 2.5O_2 \quad \text{- Xylose } 0.009 \tag{5.19}$$

$$2C_5H_{10}O_5 \rightarrow 5CH_3COOH \quad \text{- Xylose } 0.024 \tag{5.20}$$

$$3C_5H_{10}O_5 \rightarrow 5CH_3CHOHCOOH \quad \text{- Xylose } 0.014 \tag{5.21}$$

### 5.2.2.2 Mixture Analysis

Considering all the reactions obtained from the reaction analysis step the total number of compounds selected for this synthesis problem is increased to 13. All the compounds selected are given in Table 34.

*Table 34: Separation techniques identified for each binary pair in the synthesis problem*

| Compound | Label |
|---|---|
| Oxygen | A |
| Carbon dioxide | B |
| Ethanol | C |
| Water | D |
| CSL | E |
| Acetic acid | F |
| Furfural | G |
| Lactic acid | H |
| HMF | I |
| Glycerol | J |
| Succinic acid | K |
| SS (soluble solids) | L |
| IS (insoluble solids) | M |

Here to simplify the problem all the sugars (glucose, xylose, cellobiose, arabinose, mannose, and galactose) present in the problem are lumped into single pseudo component as soluble solids. Similarly, all the solids present in the problem (cellulose, hemicellulose, arabinan, mannan, galactan, lignin, cellulose, and biomass) are lumped into single pseudo component as insoluble solids. The pure component properties for the compounds is shown in the Table 35 and binary ratio matrix generated for this problem is given in Table 36.

*Table 35: Pure component properties in the synthesis problem. Refer to Table 4 for annotations*

| | **C** | **D** | **F** | **G** | **H** | **J** |
|---|---|---|---|---|---|---|
| $M_w$ (g/mol) | 46.069 | 18.015 | 60.053 | 96.086 | 90.079 | 92.095 |
| $\omega$ | 0.6452 | 0.3449 | 0.4665 | 0.3678 | 1.0221 | 1.0335 |
| $T_c$ (K) | 513.92 | 647.13 | 591.95 | 670.15 | 675 | 723 |
| $P_c$ (bar) | 60.676 | 217.666 | 57.103 | 55.86 | 58.821 | 20.923 |
| $Z_c$ | 0.24 | 0.229 | 0.211 | 0.256 | 0.267 | 0.0931 |
| $V_c$ ($m^3$/kmol) | 0.2 | 0.1 | 0.2 | 0.3 | 0.3 | 0.3 |
| $T_b$ (K) | 351.44 | 373.15 | 391.05 | 434.85 | 490 | 561 |
| $d_m$ $\times 1 \cdot 10^{-30}$ (C · m) | 1.6906 | 1.8495 | 1.7386 | 3.5971 | 1.1391 | 4.1966 |
| $r_g$ (Å) | 2.259 | 0.615 | 2.61 | 3.35 | 3.298 | 3.52 |
| $T_m$ (K) | 159.05 | 273.15 | 289.81 | 236.65 | 289.9 | 291.33 |
| $T_{tp}$ (K) | 159.05 | 273.16 | 289.81 | 236.65 | 289.9 | 291.33 |
| $P_{tp}$ (Pa) | 4.78E-09 | 6.04E-03 | 1.26E-02 | 1.53E-05 | 1.64E-06 | 9.18E-08 |
| $M_v$ ($m^3$/kmol) | 5.86E-02 | 1.81E-02 | 5.76E-02 | 8.32E-02 | 7.38E-02 | 7.34E-02 |
| $H_f$ (kJ/kmol) | -2.35E+05 | -2.42E+05 | -4.3E+05 | -1.51E+05 | -6.00E+05 | -5.83E+05 |
| $G_f$ (kJ/kmol) | -1.68E+05 | -2.29E+05 | -3.8E+05 | -1.03E+05 | -5.21E+05 | -4.48E+05 |
| $S_{IG}$ (kJ/kmol · K) | 2.81E+02 | 1.89E+02 | 2.83E+02 | 3.33E+02 | 4.53E+02 | 3.96E+02 |
| $H_{fus}$ (kJ/kmol) | 4.93E+03 | 6.00E+03 | 1.17E+04 | 1.44E+04 | 1.13E+04 | 1.83E+04 |
| $H_{comb}$ (kJ/kmol) | -1.2E+06 | 0.00E+00 | -8.2E+05 | -2.2E+06 | -1.23E+06 | -1.4E+06 |
| $\delta$ ($\sqrt{}$ kJ/$m^3$) | 26.1333 | 47.8127 | 19.0078 | 23.6099 | 33.1095 | 34.1191 |
| $V_{vw}$ ($m^3$/kmol) | 0.0319 | 0.0124 | 0.0333 | 0.0481 | 0.048 | 0.0514 |
| $A_{vw}$ ($m^2$/kmol) | 4.93E+08 | 2.26E+08 | 5.18E+08 | 6.21E+08 | 7.20E+08 | 7.65E+08 |
| $P_{nvap}$ (Pa) | 7.92E+03 | 3.17E+03 | 2.08E+03 | 3.00E+02 | 4.72E-01 | 2.18E-02 |

*Table 36: Binary ratio matrix for a select set of properties. Tb - normal boiling point, RG - radius of gyration, Tm - normal melting point, Mv - molar volume, SolPar - solubility parameter, Vvw - Van der Waals volume, Pnvap - vapor pressure*

| **Binary pair** | | **Tb** | **RG** | **Tm** | **Mv** | **SolPar** | **Vvw** | **Pnvap** |
|---|---|---|---|---|---|---|---|---|
| **A** | B | 1.81 | 1.53 | 3.98 | 1.33 | 1.78 | 1.52 | 4.65 |
| | C | 3.9 | 3.32 | 2.93 | 2.09 | 3.19 | 2.46 | 3782.96 |
| | D | 4.14 | 1.11 | 5.02 | 1.55 | 5.84 | 1.05 | 9459.83 |
| | F | 4.34 | 3.84 | 5.33 | 2.06 | 2.32 | 2.56 | 14423.75 |
| | G | 4.82 | 4.93 | 4.35 | 2.97 | 2.89 | 3.7 | Very high |
| | H | 5.43 | 4.85 | 5.33 | 2.63 | 4.05 | 3.69 | Very high |
| | I | 6.45 | 5.82 | 7.49 | 5.37 | 2.68 | 4.81 | Very high |
| **B** | C | 1.80 | 2.17 | 1.36 | 1.57 | 1.79 | 1.62 | 813.91 |
| | D | 1.91 | 1.69 | 1.26 | 2.06 | 3.28 | 1.59 | 2035.28 |
| | F | 2.01 | 2.51 | 1.34 | 1.55 | 1.31 | 1.69 | 3103.27 |
| | G | 2.23 | 3.22 | 1.09 | 2.23 | 1.62 | 2.44 | Very high |
| | H | 2.51 | 3.17 | 1.34 | 1.98 | 2.27 | 2.44 | Very high |
| | I | 2.98 | 3.81 | 1.88 | 4.04 | 1.51 | 3.17 | Very high |
| **C** | D | 1.06 | 3.67 | 1.72 | 3.24 | 1.83 | 2.58 | 2.5 |
| | F | 1.11 | 1.16 | 1.82 | 1.02 | 1.37 | 1.04 | 3.81 |
| | G | 1.24 | 1.48 | 1.49 | 1.42 | 1.11 | 1.5 | 26.43 |
| | H | 1.39 | 1.46 | 1.82 | 1.26 | 1.27 | 1.5 | Very high |
| | I | 1.66 | 1.75 | 2.56 | 2.57 | 1.19 | 1.96 | Very high |
| **D** | F | 1.05 | 4.24 | 1.06 | 3.19 | 2.52 | 2.69 | 1.52 |
| | G | 1.17 | 5.45 | 1.15 | 4.61 | 2.03 | 3.89 | 10.57 |
| | H | 1.31 | 5.36 | 1.06 | 4.08 | 1.44 | 3.88 | 6705.31 |
| | I | 1.56 | 6.44 | 1.49 | 8.33 | 2.18 | 5.05 | Very high |
| **F** | G | 1.11 | 1.28 | 1.22 | 1.44 | 1.24 | 1.44 | 6.93 |
| | H | 1.25 | 1.26 | 1 | 1.28 | 1.74 | 1.44 | 4397.68 |
| | I | 1.49 | 1.52 | 1.4 | 2.61 | 1.15 | 1.88 | Very high |
| **G** | H | 1.13 | 1.02 | 1.23 | 1.13 | 1.4 | 1 | 634.42 |
| | I | 1.34 | 1.18 | 1.72 | 1.81 | 1.08 | 1.3 | Very high |

Azeotropic analysis of the mixture using azeopro identified 3 binary azeotropes in the system (as shown in Table 37). Since only ethanol is product which needs to be separated and water is not being recycled back in the synthesis problem, only the first azeotrope involving water and ethanol is considered for further analysis. Azeopro also suggested ethylene glycol and benzene as potential mass separating agents to separate water and ethanol through extractive and azeotropic distillation respectively.

*Table 37: Azeotropic data for the synthesis problem*

| X1 | X2 | Tboil (K) | Press (atm) | X1 (mf) |
|---|---|---|---|---|
| Ethanol | Water | 352.5 | 1 | 0.8628 |
| Water | Acetic-Acid | 371.97 | 1 | 0.8384 |
| Water | Furfural | 371.14 | 1 | 0.894 |

In this case study, a new solvent is designed to separate the ethanol-water azeotrope using the liquid-liquid extraction process using ProCAMD tool. The desired properties of the solvent are given in the Table 38, based upon which, molecules are generated to match the properties.

*Table 38 : Desired properties of the solvent for liq-liq extraction of ethanol*

| Desired Characterstics of the solvent | | |
|---|---|---|
| **Property** | **Target value** | **Comments** |
| Solubility parameter | 17 < SP < 22 | Since Ethanol solubility parameter is 20.3 Mpa$^{0.5}$ |
| Boiling point | $T_b$ > 400 K | Easy recovery of solvent |
| Melting point | $T_m$<270 K | liquid state of the solvent near operating conditions |
| Selectivity | Sel > 50 | Ensure good separation |
| Azeotrope | No azeotrope with Ethanol | Easy recovery of solvent |
| Miscibility | Immiscibile with Feed | Ensure 2 phase generation |

A total of 46 different solvents were designed by the ProCAMD matching the desired properties. The solvent with highest selectivity, 1-heptanal was chosen for further analysis. Figure 61 confirms the possibility of formation of two phases between water and solvent.

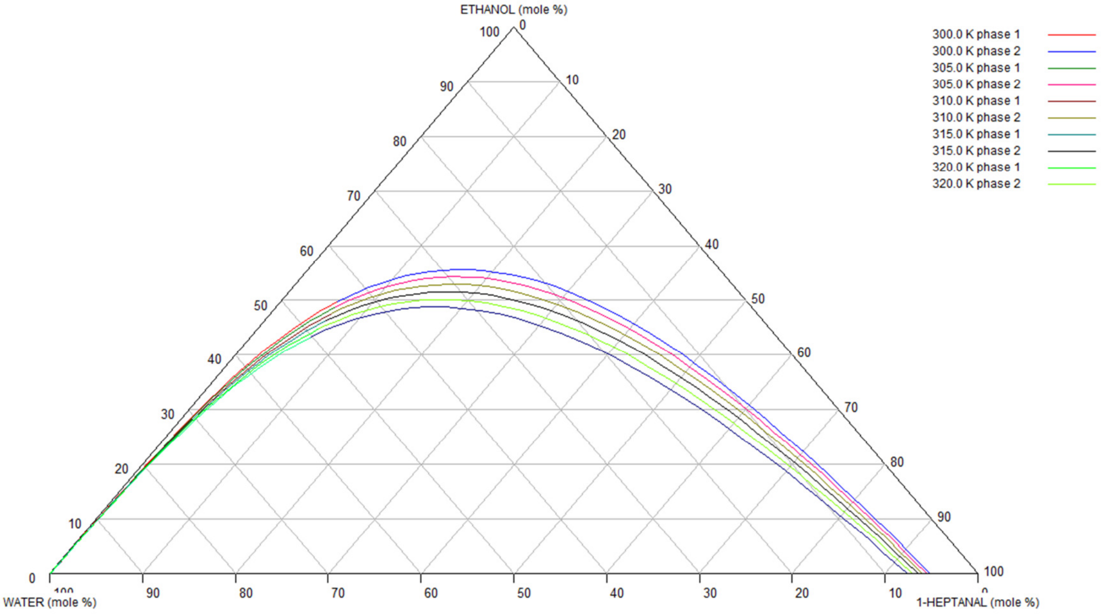


*Figure 61: Ternary plot 1-Heptanal, Water and Ethanol using ICAS.*

#### 5.2.2.3 Feasible Separation Task Analysis

Table 39 shows the feasible separation techniques to separate each of the binary pairs for the synthesis problem. As per the synthesis problem definition, only ethanol is considered as product so it's not necessary to consider all separation tasks and corresponding techniques. Separation of insoluble solids after the reactor is carried using decantation.

*Table 39: Separation techniques identified for binary pairs in the synthesis problem. S* represents the solvent*

| Binary pair | Separation Tasks Identified |
|---|---|
| B/C | Distillation, Flash |
| D/J | Flash, Liquid membrane, Pervaporation |
| D/C | Crystallization, Distillation, Liq membrane, Pervaporation, Ext.distillation, Liq-Liq extraction, Azeotropic distillation, Gas adsorption |
| D/F | Absorption, Gas Adsorption, Distillation, Liq membrane, Prevaporation, Liq Adsorbtion |
| D/K | Crystallization, Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| J/C | Crystallization, Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| J/F | Liq membrane, Pervaporation, Liq Adsorbtion, Flash |
| J/K | Liq membrane, Pervaporation, Liq Adsorbtion, Crystallization |
| J/H | Liq membrane, Pervaporation, Liq Adsorbtion, Flash |
| C/F | Crystallization, Distillation, Liq membrane, Pervaporation |
| C/K | Crystallization, Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| C/H | Crystallization, Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| F/K | Crystallization, Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| F/H | Flash, Liq membrane, Pervaporation, Liq Adsorbtion |
| K/H | Crystallization, Liq membrane, Pervaporation, Liq Adsorbtion |
| S*/C | Distillation, Pervaporation, Evaporation |
| S*/D | Pervaporation, Distillation |

### 5.2.3 Step 3 Process-groups Selection:

From the design problem analysis, all the needed information is available to represent the process flowsheet with process groups.

- Inlet and Outlet process-groups: From the problem definition step, two inlet process-groups, representing the cellulose stream and the enzymes, are identified. Two outlet process-groups, representing the ethanol and the waste streams, are also selected for this synthesis problem.

- Reactor process-group: The scarification and fermentation reactions have been identified. The reaction is performed in a single reactor. From the problem analysis, the reaction, together with the conversion, is known. The reactor can be represented with a conversion-based reactor process-group.

- Separation process-groups: From the separation task identification analysis carried out in step 5.2.2.3, all feasible separation tasks applicable to the synthesis problem are identified, as shown in Table 39. Using this, information process groups representing the separation tasks are retrieved from the process-groups database. These selected process-groups are initialized with all possible combinations of chemical species. Table 40 shows all the initialized process groups for production of bioethanol.

*Table 40: Initialized process groups for the synthesis problem.*

| **Operation type** | |
|---|---|
| Pervaporation | pvD/CEF,pvC/DEF,pvC/S,pvC/D,pvC/E |
| Molecular-sieve separation | msC/D |
| Distillation | dlAB/CDEF,dlCD/DEF,dlC/E,dlC/S, |
| Crystallization | crE/C,crE/D,crE/CD,crEC/D,crC/D |
| Decantation | dcABCDEF/M |
| Inlet /Outlet | iL,iM,oC,oD |
| Reactor | rLM/ABCDEFM |
| Cyclic groups | (llCS/DEF)(pvC/S), (llCS/DEF)(dlC/S), (llCS/DEF)(lmC/S), (llCS/DEF)(lmCD/S),(llCS/DEF)(pvCD/S),(llCS/DEF)(dlCD/S),(llCS/DEF)(pvCS/D),(azC/SD)(pvS/D) ,(azC/SD)(dlS/D), (azC/SD)(lmS/D),(edC/SD)(pvS/D),(edC/SD)(dlS/D), (edC/SD)(lmS/D) |

## 5.2.4 Step 4 Generation of Flowsheets:

This step is carried in two tasks.

### 5.2.4.1 Superstructure generation

Based on the 34 initialized process groups, the superstructure of all the alternatives is generated using the flowsheet generation method. Figure 62 represents superstructure of all feasible alternatives for the bioethanol synthesis problem. The superstructure represents a total of 92 structurally feasible alternatives for producing bioethanol from lignocellulosic raw material.

### 5.2.4.2 Generation of SFILES

All the identified process alternatives are converted into SFILES, which store the structural information of the alternatives. SFILES representations of selected alternatives are given in

Table 41. All the SFILES represent the downstream separation part of the process. For all the alternatives generated refer to Table E1 (Appendix E).

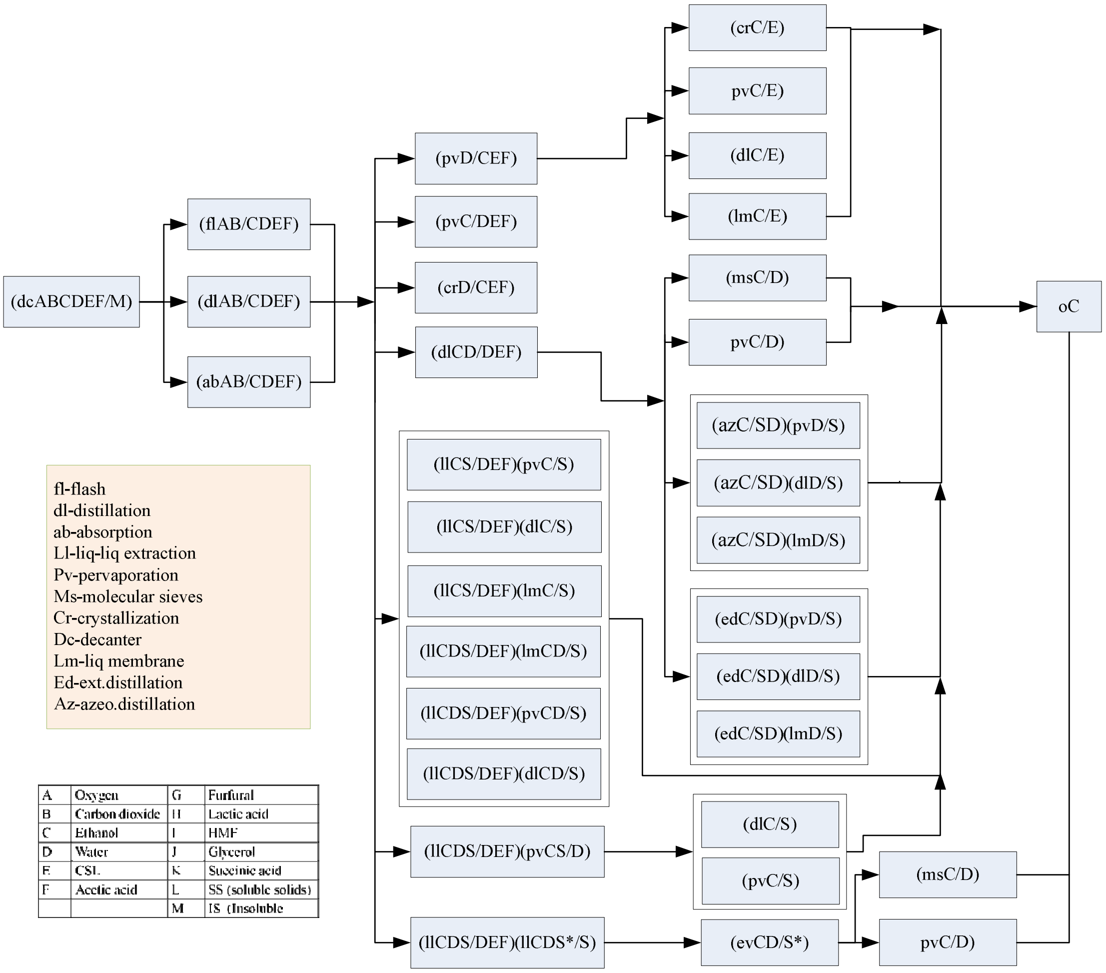


*Figure 62: Superstructure of alternatives for Bioethanol synthesis problem*

*Table 41: Process alternatives generated for bioethanol production*

| SNO | SFILES |
|---|---|
| 1 | (dcABCDEF/M)(flAB/CDEF)(pvC/DEF)(oC) |
| 2 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(crC/E)(oC) |
| 3 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(pvC/E)(oC) |
| 4 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(dlC/E)(oC) |
| 5 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(lmC/E)(oC) |
| 6 | (dcABCDEF/M)(flAB/CDEF)(crD/CEF)(crC/E)(oC) |
| 10 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(msC/D)(oC) |
| 11 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(pvC/D)(oC) |
| 16 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](dlD/S) |
| 46 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCS/D)(dlC/S)(oC) |

### 5.2.5 Step 5 Ranking of Flowsheets:

Table 42 provides the top four process alternatives ranked with respect to energy consumption of the process. Energy consumption for the alternatives is calculated using the energy index flowsheet property model as described in section 2.2.2.4. In addition to using the energy index, the purity of ethanol product stream and carbon foot print is also estimated using the flowsheet property models.

*Table 42: Top ranked process alternatives for the synthesis problem.*

| **Design No** | **Energy Index** | **Ethanol Purity** (mol %) | **Carbon Footprint** ($CO_2$ Eq) |
|---|---|---|---|
| 46 | 0.02062 | 99.5 | 0.0450 |
| 10 | 0.03616 | 99.8 | 0.0789 |
| 11 | 0.03616 | 99.8 | 0.0789 |
| 16 | 0.10242 | 99.5 | 0.2236 |

### 5.2.6 Step 6 Process Design:

Mass resolution of all the selected designs is carried out using simple models of mixers and splitters. Similarly, an enthalpy balance is applied across each unit operation in each alternative to estimate the total energy required by the process. Table 43 represents the mass and energy balance results of the selected designs.

*Table 43: Mass and Energy balance for selected alternatives*

| **Design No** | **Ethanol** (Kmol/hr) | **Utilities** (MKj/hr) |
|---|---|---|
| 46 | 444.5 | 83.81 |
| 10 | 443.5 | 94.77 |
| 11 | 443.5 | 94.77 |
| 16 | 442 | 123.09 |

Design parameters of the unit operations present in the process alternatives are calculated using the reverse simulation method. Table 44 gives the design data for the distillation columns present in the in the top two alternatives (design no 46, 10).

*Table 44: Design of distillation column using driving force method.*

| **Distillation column design (driving force method)** | **Design 46 Solvent recovery** | **Design 10 Beer column** |
|---|---|---|
| Given a NC component process group | 2 | 2 |
| Order the components with respect to relative volatility | C/S | CD/D |
| Driving force between the key components FDimax ,Di | 0.71, 0.1 | 0.35 , 0.12 |
| Recovery of light key | 0.998 | 0.99 |
| Recovery of heavy key | 0.999 | 0.99 |
| $N_{ideal * 1.5}$ | 15 | 21 |
| $N_f$ Feed location | 12 | 10 |

## 5.2.7 Step 7 Rigorous Simulation:

The process designs 46, 10 and 16 are selected for rigorous simulation by means of a commercial process simulator (PROII). The first process alternative is a novel processing route for production of bioethanol. Alternatively, designs 10 and 16 are similar to the processing routes proposed in literature.

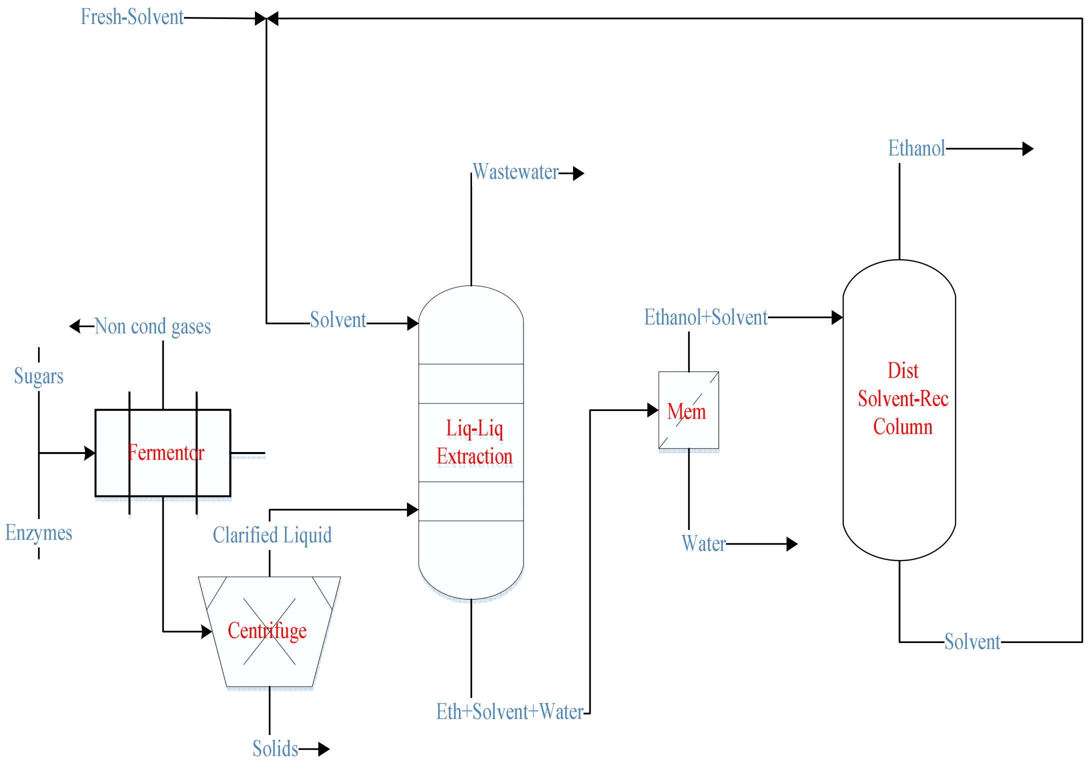


*Figure 63: Process flowsheet for generated alternative 1 (design 46)*

Process Alternative 1 (design 46): In this alternative, the dehydration of ethanol is done using liquid-liquid extraction process. The designed solvent 1-heptanal is used to extract ethanol from the fermentation mixture in extraction column where ethanol is concentrated from 6 wt% to 88 wt%. The remaining water is removed using a hydrophilic pervaporation membrane (Kujawski 2000) which has high selectivity and preferential affinity for water. Finally, in the last separation task, distillation is used to separate the solvent from ethanol and recycle it back to the extraction column. The downstream separation of the process is shown in Figure 63 and Table 45 gives the stream summary of the process.

*Table 45: Stream summary for process alternative 1 (design 46)*

| Stream Name | Clarified Liq | Fresh-Sol | Sol-Rec | Water | Ethanol |
|---|---|---|---|---|---|
| Temperature (K) | 303.37 | 298.00 | 298.00 | 340.00 | 351.54 |
| Pressure (atm) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Rate (Kg-mol/hr) | 17840.37 | 7.82 | 2462.24 | 187.27 | 446.83 |
| ETHANOL | 449.026 | 0.000 | 0.445 | 0.445 | 444.185 |
| WATER | 17226.086 | 0.000 | 0.000 | 177.048 | 0.177 |
| C6 | 12.896 | 0.000 | 0.000 | 0.035 | 0.000 |
| C5 | 10.656 | 0.000 | 0.000 | 0.052 | 0.000 |
| C5A | 3.471 | 0.000 | 0.000 | 0.017 | 0.000 |
| C6M | 14.068 | 0.000 | 0.000 | 0.038 | 0.000 |
| G6G | 0.859 | 0.000 | 0.000 | 0.002 | 0.000 |
| C12 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| CLS | 87.315 | 0.000 | 0.000 | 0.897 | 0.001 |
| ACETACID | 18.226 | 0.000 | 0.005 | 4.927 | 0.000 |
| SULFURIC | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| FURFURAL | 1.556 | 0.000 | 0.002 | 1.544 | 0.000 |
| HMF | 0.770 | 0.000 | 0.001 | 0.764 | 0.000 |
| CO2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| O2 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| NH3 | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| XYLITOL | 0.000 | 0.000 | 0.000 | 0.000 | 0.000 |
| LACACID | 14.864 | 0.000 | 0.001 | 1.323 | 0.000 |
| SUCCNAC | 0.424 | 0.000 | 0.000 | 0.022 | 0.000 |
| GLYCEROL | 0.153 | 0.000 | 0.000 | 0.152 | 0.000 |
| HEPTANAL | 0.000 | 7.824 | 2461.790 | 0.000 | 2.465 |

Process Alternative 2 (design 10): In this alternative, the anhydrous ethanol is produced using molecular sieves. Similar designs using different types of molecular sieves with pore size 3Å and 4Å are proposed by many researchers (Sowerby and Crittenden 1988; Trent 1993). In this process, distillation is used to concentrate the ethanol composition from 6 wt% to 85 wt%. Then, the molecular sieve absorption technique is used to dry the ethanol in the last separation task. Figure 64 gives the schematic diagram of the downstream separation process for bioethanol using molecular sieves. Table 46 gives the stream summary of the process.

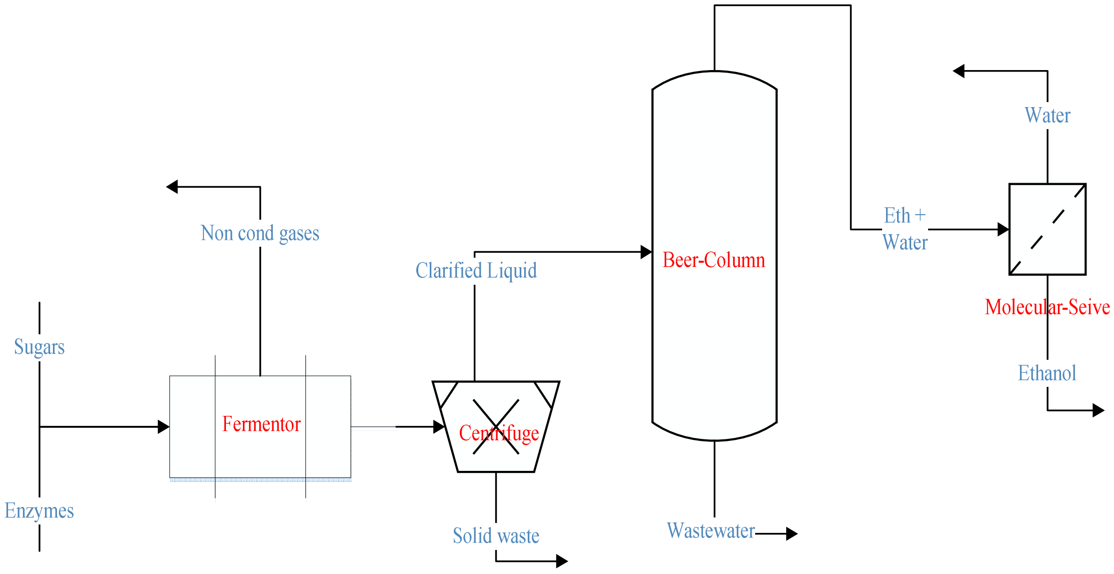


*Figure 64: Process flowsheet for generated alternative 2 (design 10)*

*Table 46: Stream summary for process alternative 2 (design 10)*

| **Stream Name** | **Clarified-Liq** | **Wastewater** | **Eth-water** | **Ethanol** | **Water** |
|---|---|---|---|---|---|
| Temperature (K) | 303.37 | 373.23 | 352.25 | 351.58 | 372.85 |
| Pressure (atm) | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 |
| Rate (Kgmol/hr) | 17840.37 | 17205.32 | 635.05 | 442.50 | 192.55 |
| ETHANOL | 449.03 | 4.49 | 444.53 | 442.31 | 2.22 |
| WATER | 17226.08 | 17035.97 | 190.12 | 0.19 | 189.93 |
| C6 | 12.90 | 12.90 | 0.00 | 0.00 | 0.00 |
| C5 | 10.66 | 10.66 | 0.00 | 0.00 | 0.00 |
| C5A | 3.47 | 3.47 | 0.00 | 0.00 | 0.00 |
| C6M | 14.07 | 14.07 | 0.00 | 0.00 | 0.00 |
| G6G | 0.86 | 0.86 | 0.00 | 0.00 | 0.00 |
| C12 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CLS | 87.31 | 87.31 | 0.01 | 0.00 | 0.01 |
| ACETACID | 18.23 | 17.88 | 0.34 | 0.00 | 0.34 |
| SULFURIC | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| FURFURAL | 1.56 | 1.50 | 0.05 | 0.00 | 0.05 |
| HMF | 0.77 | 0.77 | 0.00 | 0.00 | 0.00 |
| CO2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| O2 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| NH3 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| XYLITOL | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| LACACID | 14.86 | 14.86 | 0.00 | 0.00 | 0.00 |
| SUCCNAC | 0.42 | 0.42 | 0.00 | 0.00 | 0.00 |
| GLYCEROL | 0.15 | 0.15 | 0.00 | 0.00 | 0.00 |

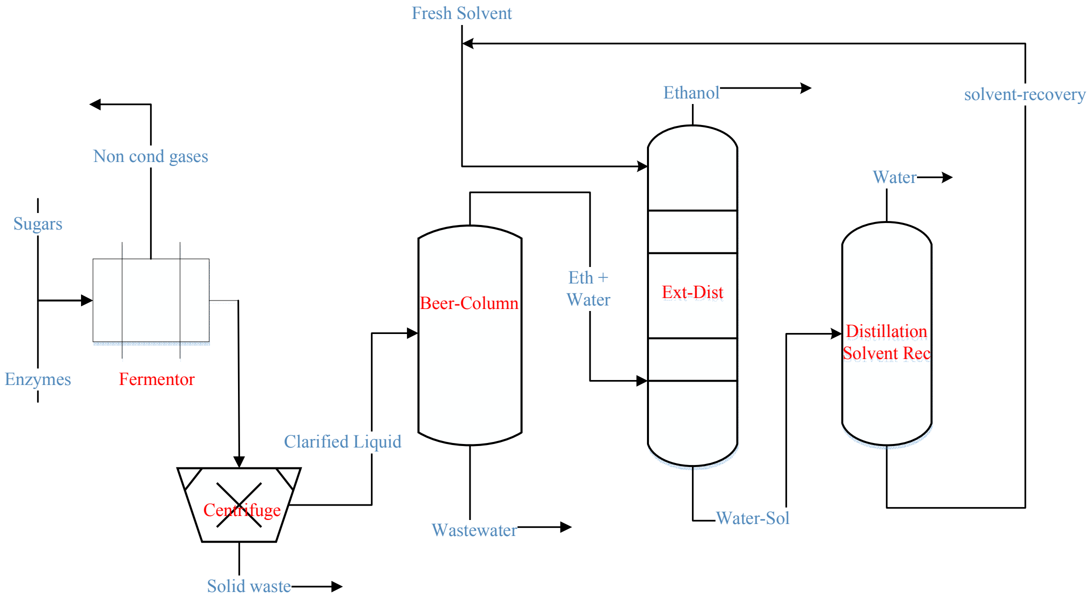


*Figure 65: Process flowsheet for generated alternative 3 (design 16)*

Process Alternative 3 (design 16): This design represents the traditional way to produce anhydrous ethanol using ethylene glycol as an entrainer in extractive distillation setup as shown in Figure 65. Using glycols as entrainers was proposed by many researchers (Robert H. Perry and Don W. Green 2008; Meirelles, Weiss, and Herfurth 2007). In this process, the clarified liquid from the centrifuge is sent distillation column to concentrate the ethanol composition from 6 wt% to 85 wt%. The concentrated ethanol is sent to extractive distillation unit where the high boiling solvent (ethylene glycol) is used as an entrainer. In this column, the solvent interacts with water and ethanol differently, which will change the relative volatility of the water-ethanol mixture. Pure ethanol is removed as distillate from the extractive column and the solvent and water mixture is sent to recovery column where solvent is recovered as bottoms product and recycled back.

The first process alternative obtained has the least energy consumption when compared to the literature designs. The top alternative generated by this method has 37 % lower energy requirements when compared to the second best alternative. This is because the beer column, which is the most energy consuming unit operation in the whole ethanol process, is avoided in the 1st alternative. Table 47 gives the energy comparisions of the top 3 alternatives.

*Table 47: Comparison of energy requirements and production rates for 3 process alternatives*

| | **Cooling** M Kj/hr | **Heating** M Kj/hr | **Ethanol** Kgmol/hr | **Novel solution** |
|---|---|---|---|---|
| Design 46 | -26.15 | 109.9 | 446.828 | yes |
| Design 10 | -62.04 | 156.8 | 442.5 | no |
| Design 16 | -159.08 | 254.07 | 444.535 | no |

## 5.3 SEPARATION OF ALKANE ISOMERS

### 5.3.1 Step 1 Synthesis Problem Definition:

The synthesis problem definition is to separate a 5-component alkanes mixture into its constituent pure compound products. The structural definition of the synthesis problem is as follows: 1 inlet of alkane mixture feed and 5 outlets for the individual product streams as shown in Figure 66.

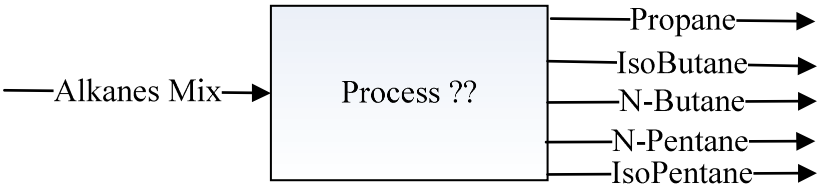


*Figure 66: Structural definition of the synthesis problem*

Table 48 gives stream composition, temperature and pressure information for the inlet feed stream. The design constraint for this synthesis problem is that the minimum purity of all the product streams should be 99.5 mol %.

*Table 48: Inlet stream conditions*

| | | **Inlet 1** |
|---|---|---|
| Temperature | K | 347.02 |
| Pressure | atm | 6.00 |
| Flow Rates | kg-mol/hr | |
| (A) PROPANE | | 45.40 |
| (B) IBUTANE | | 136.10 |
| (C) BUTANE | | 226.80 |
| (D) IPENTANE | | 181.40 |
| (E) PENTANE | | 317.50 |

The flowsheet property specification or the performance criteria for this problem is the total energy consumption for the process.

### 5.3.2 Step 2 Problem Analysis:

In this step all the necessary information required to solve the synthesis problem is generated. This is carried out in 3 tasks: i) reaction analysis, ii) mixture analysis and iii) feasible separation task identification.

#### 5.3.2.1 Reaction Analysis

Since all the compounds present in the outlet streams are present in the inlet/feed stream indicates that no reaction is required for this synthesis problem.

### 5.3.2.2 Mixture Analysis

The analysis of the pure component properties in the process design problem is performed after retrieving the 22 pure component properties of the chemical components from the compound property database. The pure components properties of all the compounds identified in the synthesis problem are listed in the Table 49.

*Table 49: Pure component properties in the synthesis problem. Refer to Table 4 for annotations*

| **Property** | **A** | **B** | **C** | **D** | **E** |
|---|---|---|---|---|---|
| $M_w$ (g/mol) | 44.10 | 58.12 | 58.12 | 72.15 | 72.15 |
| $\omega$ | 0.15 | 0.18 | 0.20 | 0.23 | 0.25 |
| $T_c$ (K) | 369.83 | 408.14 | 425.12 | 460.43 | 469.70 |
| $P_c$ (bar) | 41.92 | 36.00 | 37.46 | 33.37 | 33.26 |
| $Z_c$ | 0.28 | 0.28 | 0.27 | 0.27 | 0.27 |
| $V_c$ ($m^3$/kmol) | 0.20 | 0.30 | 0.30 | 0.30 | 0.30 |
| $T_b$ (K) | 231.11 | 261.43 | 272.65 | 300.99 | 309.22 |
| $d_m$ $\times 1\cdot 10^{-30}$ ($C \cdot m$) | 0.00 | 0.13 | 0.00 | 0.13 | 0.00 |
| $r_g$ (Å) | 2.43 | 2.95 | 2.89 | 3.32 | 3.34 |
| $T_m$ (K) | 85.47 | 113.54 | 134.86 | 113.25 | 143.42 |
| $T_{tp}$ (K) | 85.47 | 113.54 | 134.86 | 113.25 | 143.42 |
| $P_{tp}$ (Pa) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| $M_v$ ($m^3$/kmol) | 0.08 | 0.11 | 0.10 | 0.12 | 0.12 |
| $H_f$ (kJ/kmol) | -1.05E+05 | -1.34E+05 | -1.26E+05 | -1.54E+05 | -1.47E+05 |
| $G_f$ (kJ/kmol) | -2.44E+04 | -2.08E+04 | -1.67E+04 | -1.41E+04 | -8.81E+03 |
| $S_{IG}$ (kJ/kmol·K) | 270.20 | 295.39 | 309.91 | 343.74 | 349.45 |
| $H_{fus}$ (kJ/kmol) | 3.52E+03 | 4.54E+03 | 4.66E+03 | 5.15E+03 | 8.40E+03 |
| $H_{comb}$ (kJ/kmol) | -2.04E+06 | -2.65E+06 | -2.66E+06 | -3.24E+06 | -3.24E+06 |
| $\delta$ ($\sqrt{}$ kJ/$m^3$) | 13.10 | 12.57 | 13.70 | 13.86 | 14.40 |
| $V_{vw}$ ($m^3$/kmol) | 0.04 | 0.05 | 0.05 | 0.06 | 0.06 |
| $A_{vw}$ ($m^2$/kmol) | 5.59E+08 | 6.93E+08 | 6.94E+08 | 8.28E+08 | 8.29E+08 |
| $P_{nvap}$ (Pa) | 9.53E+05 | 3.52E+05 | 2.44E+05 | 9.17E+04 | 6.83E+04 |

The five compounds in the system forms 10 binary pairs. No binary azeotropes are detected in the azeotropic analysis carried out using Azeopro. The binary ratio matrix of pure component properties for all binary pairs is calculated and selected properties are shown in the Table 50.

*Table 50: Binary ratio matrix for a select set of properties. Tb - normal boiling point, RG - radius of gyration, Tm - normal melting point, Mv - molar volume, SolPar - solubility parameter, Vvw - Van der Waals volume, Pnvap - vapor pressure*

| **Binary pair** | | **Tb** | **RG** | **Tm** | **Mv** | **SolPar** | **Vvw** | **Pnvap** |
|---|---|---|---|---|---|---|---|---|
| A | B | 1.13 | 1.21 | 1.33 | 1.39 | 1.04 | 1.27 | 2.71 |
| | C | 1.18 | 1.19 | 1.58 | 1.27 | 1.05 | 1.27 | 3.91 |
| | D | 1.3 | 1.37 | 1.33 | 1.55 | 1.06 | 1.54 | 10.39 |
| | E | 1.34 | 1.37 | 1.68 | 1.53 | 1.1 | 1.54 | 13.94 |
| B | C | 1.04 | 1.02 | 1.19 | 1.09 | 1.09 | 1 | 1.44 |
| | D | 1.15 | 1.13 | 1 | 1.11 | 1.1 | 1.21 | 3.83 |
| | E | 1.18 | 1.13 | 1.26 | 1.1 | 1.15 | 1.21 | 5.14 |
| C | D | 1.1 | 1.15 | 1.19 | 1.21 | 1.01 | 1.21 | 2.65 |
| | E | 1.13 | 1.16 | 1.06 | 1.2 | 1.05 | 1.21 | 3.56 |
| D | E | 1.03 | 1 | 1.27 | 1.01 | 1.04 | 1 | 1.34 |

### 5.3.2.3 Feasible Separation Task Analysis

Feasible process operation tasks to separate each of the binary pairs are identified and Table 51 gives information on the feasible separation techniques identified for each of the binary pairs present in the synthesis problem.

*Table 51: Separation techniques identified for each binary pair in the synthesis problem*

| **Binary pair** | **Separation Tasks Identified** |
|---|---|
| A / B | Gas adsorption, Distillation |
| A / C | Gas adsorption, Distillation |
| A / D | Gas adsorption, Distillation |
| A / E | Gas adsorption, Distillation |
| B / C | Pervaporation, Distillation |
| B / D | Gas adsorption, Pervaporation, Distillation, Liquid Adsorption |
| B / E | Gas adsorption, Pervaporation, Distillation, Liquid Adsorption |
| C / D | Gas adsorption, Pervaporation, Distillation, Liquid Adsorption |
| C / E | Gas adsorption, Pervaporation, Distillation, Liquid Adsorption |
| D / E | Distillation |

## 5.3.3 Step 3 Process-groups Selection:

From the step problem analysis, all the needed information is available to represent the process flowsheet with process groups.

- Inlet and Outlet process-groups: From the problem definition step, one inlet process-group, representing the alkane feed mixture, is identified. 5 outlet process-groups, representing 5 constituent product streams, are also selected for this synthesis problem.
- Separation process-groups: From the separation task identification analysis carried out in step 5.3.2.3, all feasible separation tasks, as applicable for the synthesis problem, are identified, as shown in Table 51. Using this information, process-groups representing the separation tasks are retrieved from the process-groups database. These selected process groups are initialized with all possible combinations of chemical species. Table 52 shows all the initialized process groups for the synthesis problem.

*Table 52: Initialized process groups for the synthesis problem.*

| **Operation type** | **Process-groups** |
|---|---|
| Pervaporation | pvB/C, pvB/D, pvB/E, pvC/D, pvC/E |
| Distillation | dlA/B, dlB/C, dlC/D, dlD/E, dlC/E, dlC/D, dlB/E, dlB/D, dlA/E, dlA/D, dlA/C |
| Gas adsorption | gaA/B, gaC/D, gaC/E, gaB/E, gaB/D, gaB/C, gaA/E, gaA/D, gaA/C |
| liq adsorption | laC/D, laC/E, laB/D, laB/E |
| Inlet /Outlet | iABCDE, oA, oB, oC, oD, oE |

## 5.3.4 Step 4 Generation of Flowsheets:

Based the initialized process groups, all the structurally feasible alternatives are generated for the given separation synthesis problem. Table 47 represents selected alternatives in the form SFILES. For all the alternatives generated refer to Table F1 (Appendix F).

*Table 53: Flowsheet alternatives for the separation synthesis problem*

| **Design no** | **SFILES** |
|---|---|
| 1 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(gaED/C)(dlE/D) |
| 2 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(pvED/C)(dlE/D) |
| 3 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(laED/C)(dlE/D) |
| 4 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlED/C)(dlE/D) |
| 44 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlED/C)(dlE/D) |
| 158 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlCB/A)(dlC/B) |
| 160 | iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlC/BA)(dlB/A) |
| 176 | (iABCDE)(mABCDE)(dlEDCB/A)(dlED/CB)[(dlE/D)](dlC/B) |

## 5.3.5 Step 5 Ranking of Flowsheets:

Table 54 represents the top four process alternatives ranked with respect to energy consumption of the process. Energy consumption for the alternatives is calculated using the energy index flowsheet property model as described in section 2.2.2.4. In addition to using the energy index, the recovery of the products and carbon footprint is also estimated using the flowsheet property models.

*Table 54: Top ranked process alternatives for the synthesis problem.*

|  |  |  | Min Prod Recovery % |  |
|---|---|---|---|---|
| **Design no** | **Energy Index** | **Carbon Foot Print** | **B** | **D** |
| 176 | 0.33 | 1.48 | 0.99 | 0.99 |
| 158 | 1.35 | 10.59 | 0.99 | 0.99 |
| 44 | 2.94 | 18.65 | 0.99 | 0.99 |
| 160 | 4.01 | 22.35 | 0.99 | 0.99 |

The top ranked design (no 176) to separate the alkane mixture was proposed by Bek-Pedersen (2002) while design no 160 was proposed by Smith (1995) to separate the alkane mixture.

### 5.3.6 Step 6 Process Design:

Using simple models of splitters and mixers the mass balance is resolved and the product streams are calculated for the top ranked alternatives.

*Table 55: Mass balance for the top two alternatives*

| **Design No** | **A** kmol/hr | **B** kmol/hr | **C** kmol/hr | **D** kmol/hr | **E** kmol/hr |
|---|---|---|---|---|---|
| 176 | 45.9 | 135.9 | 227.5 | 181.1 | 317.6 |
| 158 | 45.8 | 136.1 | 226.12 | 182.3 | 316.8 |

Design parameters of the unit operations present in the process alternatives are calculated using the reverse simulation method as explained in step 2.2.5. Table 56 gives the design data for the distillation columns present in the top alternative (design 176).

*Table 56: Design of distillation column using driving force method.*

| **Distillation column design (driving force method)** | **dlA/BCDE** | **dlBC/DE** | **dlB/C** | **dlD/E** |
|---|---|---|---|---|
|  |  |  |  |  |
| Given a NC component process group | 5 | 4 | 2 | 2 |
| Order the components with respect to relative volatility | A/BCDE | BC/DE | B/C | D/E |
| Driving force between the key components FDimax ,Di | 0.24, 0.3 | 0.23 , 0.4 | 0.09, 0.5 | .07, 0.45 |
| Recovery of light key | 0.995 | 0.995 | 0.995 | 0.995 |
| Recovery of heavy key | 0.995 | 0.995 | 0.995 | 0.995 |
| Nideal * 1.5 | 17 | 17 | 45 | 74 |
| Nf Feed location | 13 | 10 | 22 | 38 |

### 5.3.7 Step 7 Rigorous Simulation:

The top ranked alternative, design number 176, is selected for final verification through rigorous simulation. Table 57 gives the stream summary for design 176, where first propane is separated from the alkane mixture, followed by a split between n-butane and isopentane. The hardest of all the separation tasks, separating the isomers of butane and pentane, is done last. Figure 67 gives the process flowsheet of the final selected design.

*Table 57: Stream summary for process alternative 1 (design no 176)*

| **Stream Name** | **Feed** | **A** | **C45mix** | **C4mix** | **B** | **C** | **D** | **E** |
|---|---|---|---|---|---|---|---|---|
| Temp (K) | 354.3 | 281.7 | 346.2 | 288.4 | 280.2 | 292.5 | 322.8 | 331.1 |
| Pres (atm) | 6 | 6 | 6 | 2 | 2 | 2 | 2 | 2 |
| Rate (kgmol/hr) | 907.20 | 45.19 | 862.01 | 363.34 | 135.88 | 227.45 | 181.04 | 317.63 |
| Fluid Rates (kgmol/hr) | | | | | | | | |
| PROPANE | 45.40 | 44.97 | 0.43 | 0.43 | 0.43 | 0.00 | 0.00 | 0.00 |
| IBUTANE | 136.10 | 0.22 | 135.88 | 135.87 | 135.20 | 0.67 | 0.01 | 0.00 |
| BUTANE | 226.80 | 0.01 | 226.79 | 226.57 | 0.25 | 226.32 | 0.23 | 0.00 |
| IPENTANE | 181.40 | 0.00 | 181.40 | 0.36 | 0.00 | 0.36 | 180.13 | 0.90 |
| PENTANE | 317.50 | 0.00 | 317.50 | 0.10 | 0.00 | 0.10 | 0.67 | 316.73 |

Table 58 gives the utilities consumption of individual unit operations in the seleted top process alterative for separation of alkane isomers.

*Table 58: Energy consumptions of all unit operations in the top ranked design*

| | **Column-1** | **Column-2** | **Column-3** | **Column-4** | **Total** |
|---|---|---|---|---|---|
| Heating MKj/hr | 35.11 | 46.69 | 37.31 | 89.07 | 208.18 |
| Cooling MKj/hr | 54.00 | 43.97 | 32.34 | 84.70 | 215.01 |

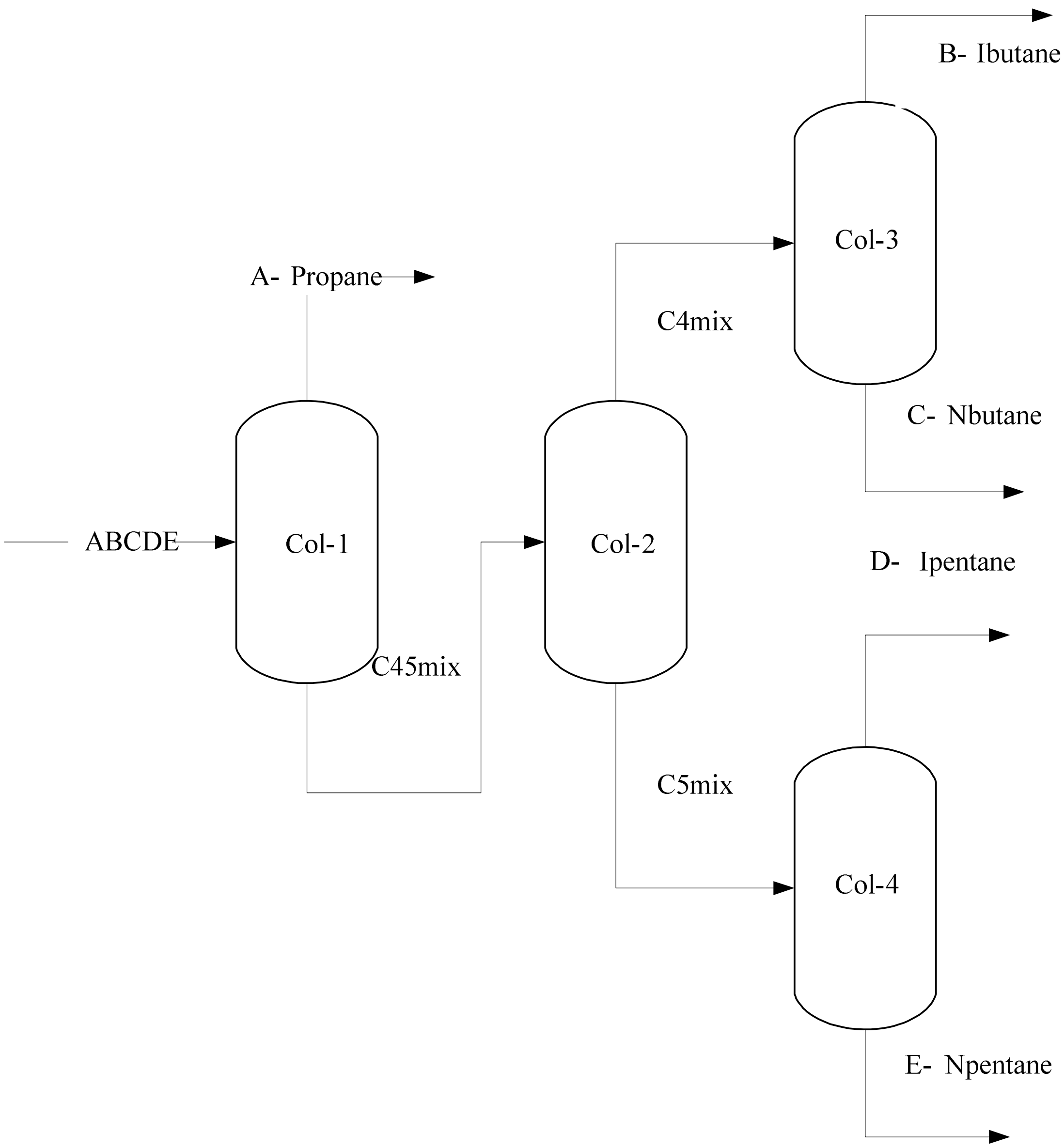


*Figure 67: Process flowsheet for generated alternative no 176*

Economic and life cycle analysis is carried on the selected alternative (design 176) to detect the process hotspots and to improve the process further. Figure 68 gives the distribution of operational costs (utilities consumption) with respect to different unit operations present in the process alternative. It is clearly evident that more than 40% of the utility cost comes from column-4. This combined with column-3 comprises more than 55% of the utilities. Since there is no waste stream in this case and no recycle streams, sustainability analysis is not considered. However, LCA analysis generated the $CO_2$ foot print with respect to each unit operation which can be seen in Figure 69.

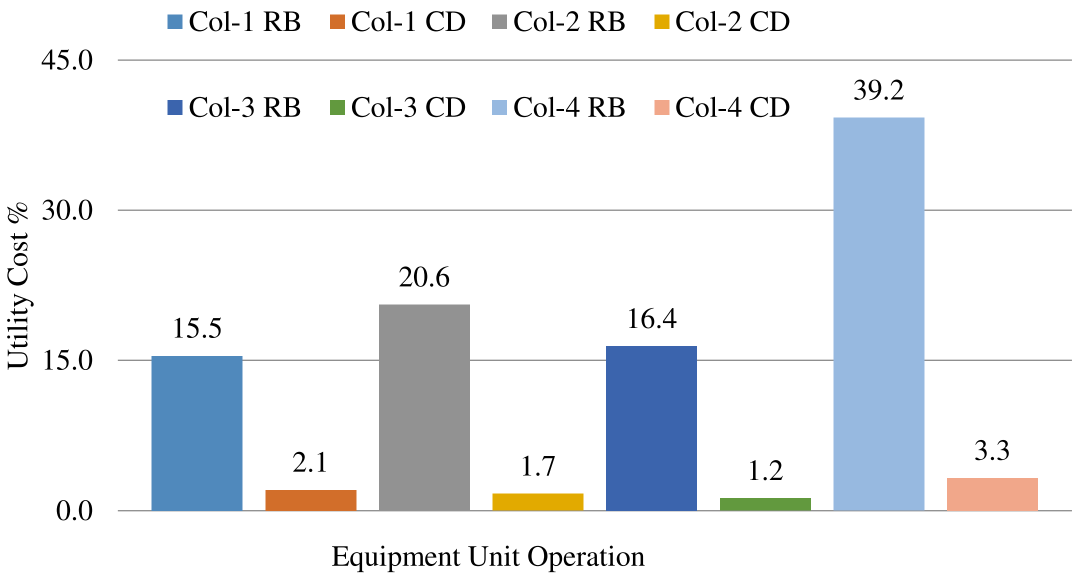


*Figure 68: Economic analysis of the selected base case design*

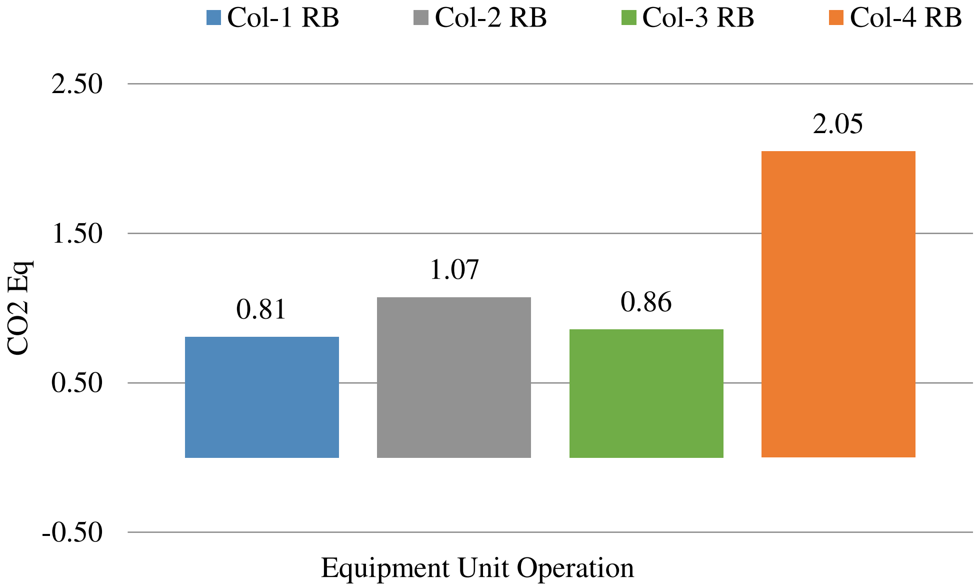


*Figure 69: Carbon Footprint of variuos equipment in selected base case design*

Based on the analysis results using Table 7 and 8 the following design targets are identified for overall improvement of the process.

- Reduce energy consumption
- Reduce utility cost
- Improvements in LCA/Sustainability indicators
- Product purity (kept as the base case)
- Reduce operational cost

### 5.3.8 Step 8 Innovative Designs:

In this case study hybrid separations method, as explained in section 2.2.7, is applied to achieve the design targets. Here the algorithm is applied to synthesize and design hybrid separation systems for both col-3 (separation of butane isomers) and col-4 (separation pentane isomers).

**Step 1:** Calculate the driving force diagram for the separation tasks: Driving force diagrams are calculated for the N-butane/Isobutane and N-pentane/Isopentane mixtures at system pressure (=2 atm). The driving force plots are shown in Figure 54 and it can be seen that the maximum driving force ($DF_{max}$) is close to 0.1 for the C4 mixture and 0.06 for the C5 mixture.

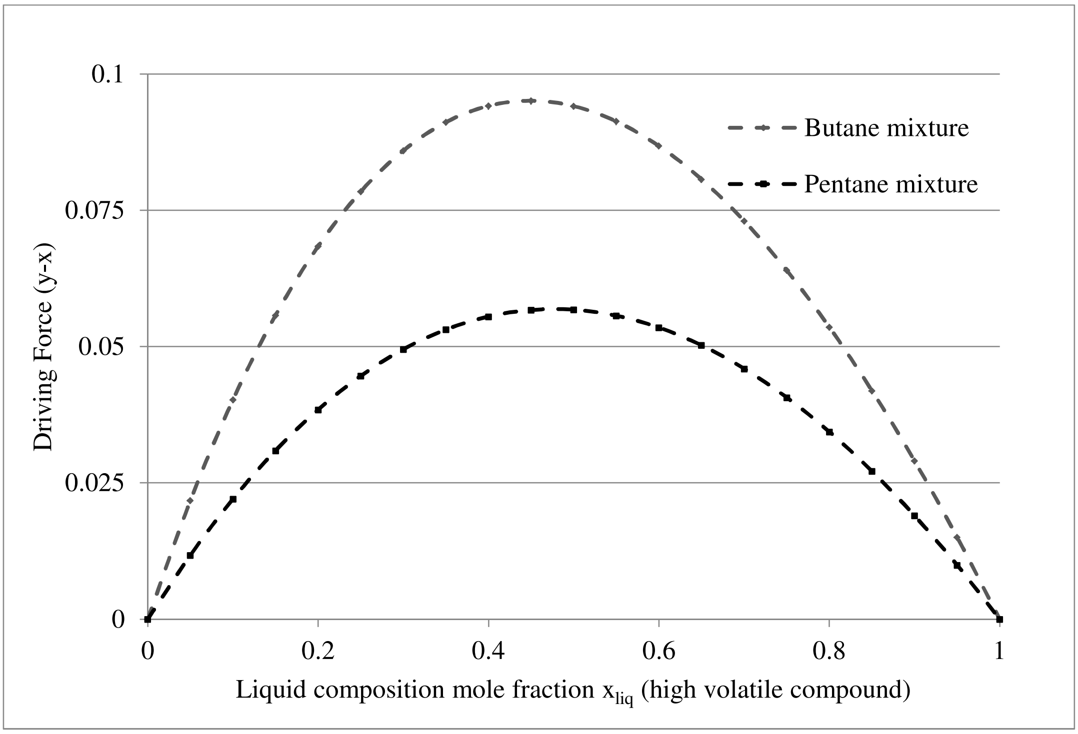


*Figure 70: Driving force diagram for C4 and C5 mixtures at 2 atm*

**Step 2:** From the knowledge-base identify the driving force close to the separation task which can represent the given system and identify $Q_{target}$ and $Q_{intermediate}$. As can be seen in Figure 71, the reboiler duties for C4 and C5 column are increasing exponentially (curve becomes increasingly steep) after 0.85 and 0.90 distillate purity until 0.995 of C4 and C5 column. So, for C4 mixture the $Q_{target} = Q_{0.995}$; and, $Q_{intermediate} = Q_{0.85}$, while for C5 mixture $Q_{target} = Q_{0.995}$ and $Q_{intermediate} = Q_{0.90}$.

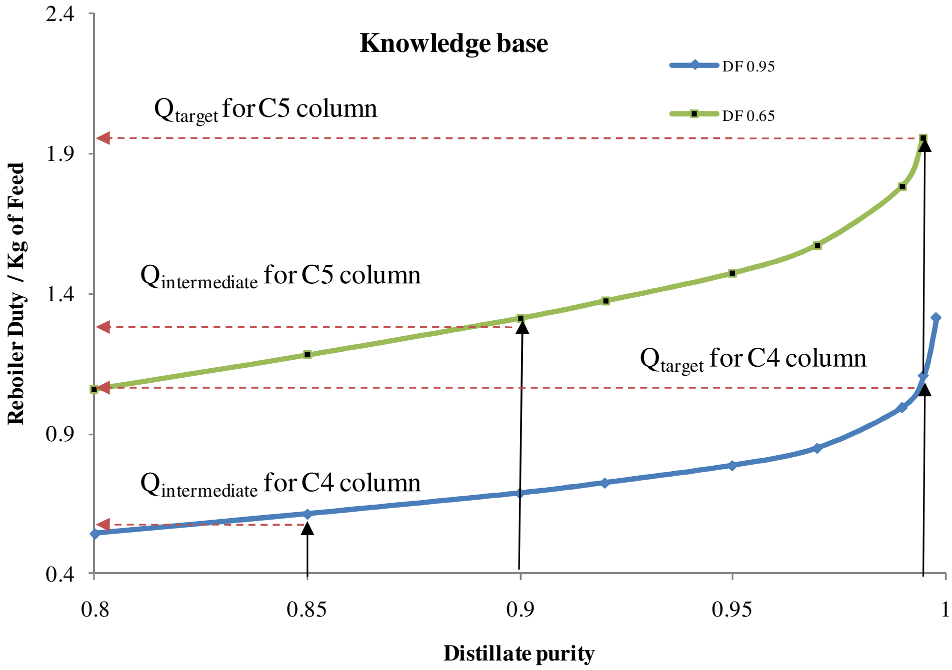


Figure 71: Knowledge base to identify $Q_{target}$ and $Q_{intermediate}$ for C4 and C5 columns.

**Step 3:** Estimate the potential energy savings using $Q_{target}$ and $Q_{intermediate}$ from step 2 using equation 2.39.

For C4 column: $Q_{target} = Q_{0.995}$ and $Q_{intermediate} = Q_{0.85}$

$$Q_{savings} = (\frac{Q_{0.995} - Q_{0.85}}{Q_{99.5}})*100$$

$$(\frac{Q_{0.995} - Q_{0.85}}{Q_{0.995}})*100 = (\frac{1.1 - 0.61}{1.1})*100 = 44.7\%$$

For C5 column: $Q_{target} = Q_{0.995}$ and $Q_{intermediate} = Q_{0.90}$

$$Q_{savings} = (\frac{Q_{0.995} - Q_{0.90}}{Q_{0.995}})*100$$

$$(\frac{Q_{0.995} - Q_{0.90}}{Q_{0.995}})*100 = (\frac{1.95 - 1.18}{1.95})*100 = 39.5\%$$

**Step 4:** Rigorous simulation with hybrid schemes for the two separation tasks (see Figure 72) are done to verify the design and final product specifications.

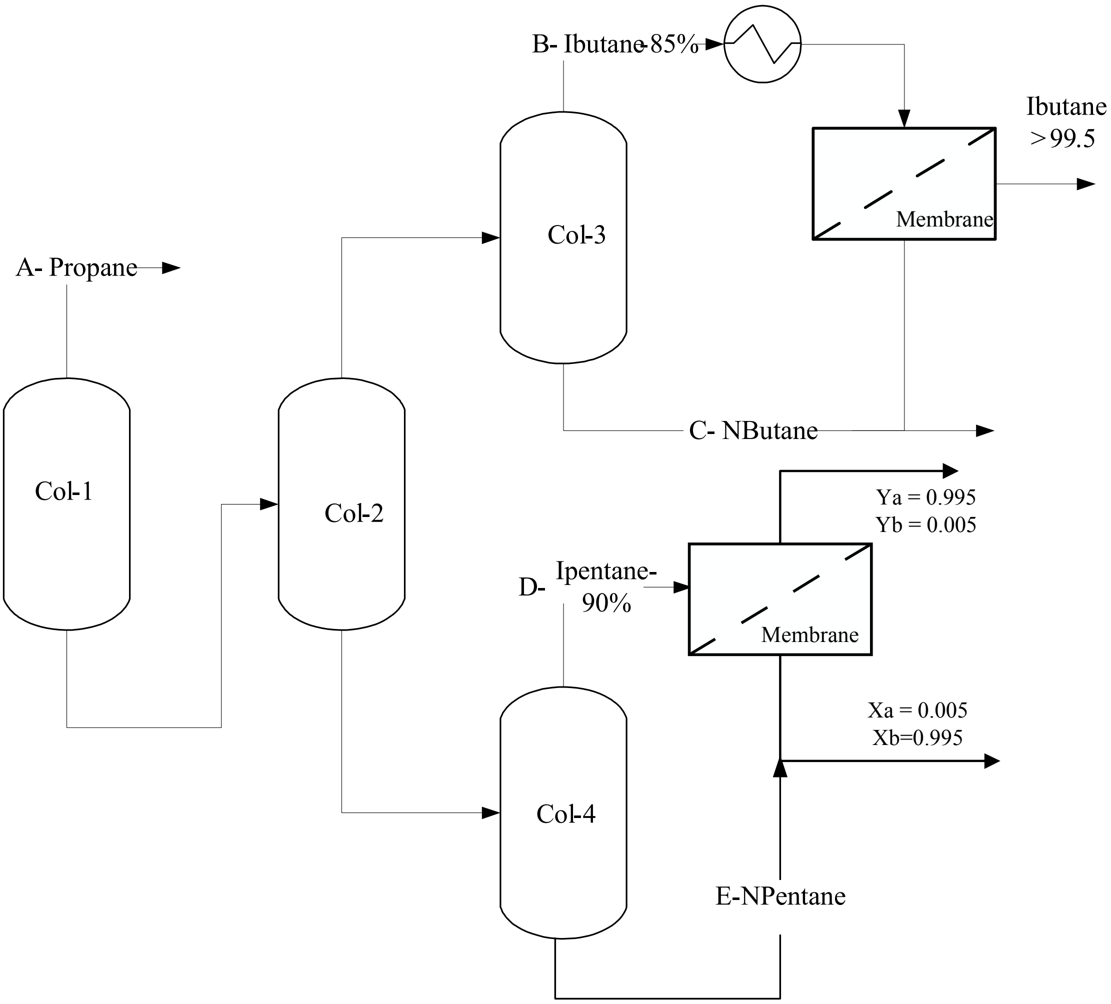


*Figure 72: New process flowsheet with hybrid schemes for separation of C4 and C5 isomers.*

From rigorous simulation of the hybrid schemes, the amount of energy saved from Col-3 and Col-4 are 44.4 % and 37.6% respectively (See Table 59), which are very close to what the method estimated using the knowledge-base.

*Table 59: Actual energy savings*

| Rigorous Simulation data (GJ/hr) | | | |
|---|---|---|---|
| | **Distillation** | **Distillation (Till region- I)** | **Savings %** |
| Energy (Col-3) | 32.33 | 17.98 | 44.4 |
| Energy (Col-4) | 89 | 55.5 | 37.6 |

**Step 5:** Membrane area required both separation tasks are estimated using results from step 4 and membrane data from literature. Data for zeolite membranes used in the design of the

membrane module (vapor permeation) to separate C4 isomers of butane from the top (vapor product) of Col-3 is given by Christophe et al. (2004). And for separation of pentane isomers membrane data given by Baudot and Bournay (2009) has been used. The membrane area required for both the separation tasks can be seen in Table 60. Also the final product purity of the butane isomers and pentane isomers are better than the base case specification of 99.5 % (mol).

*Table 60: Membrane area for C4 and C5 vapor permeation modules.*

| | **Value** | **Units** |
|---|---|---|
| Permeability of Nbutane | 0.2196 | kgmol/m$^2$ hr |
| Permeability of Isobutane | 0.0008 | kgmol/m$^2$ hr |
| Membrane Area of C4 separation | 109.24 | m$^2$ |
| Isobutane purity | 99.7 | mol % |
| Nbutane purity | 99.5 | mol % |
| | | |
| Permeability of Pentane | 0.0249 | kgmol/m$^2$ hr |
| Permeability of Isopentane | 0.001108801 | kgmol/m$^2$ hr |
| Membrane Area of C5 separation | 1297.6 | m$^2$ |
| Isopentane purity | 99.9 | mol % |
| Pentane purity | 99.5 | mol % |

### 5.3.9 Capital cost analysis for the membrane modules:

Since in the hybrid separation scheme, there is a new unit operation (membrane) when compared to base case process flowsheet, analysis has been made for the payback period related to the extra capital investment for the membrane module. Table 61 gives the calculated payback period for the capital investment using the operational savings (utility savings) of the distillation column. At the current price of 2000 – 3000 Euro/m2 for a zeolite membrane (Tennison 2001), the payback period of the membrane unit used in butane isomer hybrid scheme is close to 4 months, which is very low and makes the hybrid scheme economically feasible. While the payback period for the membrane unit for the pentane isomer separation column is close to 1.4 years, which can be further reduced by using other membranes with higher flux. For the entire process the payback period for the both membrane units together is at 1.05 yrs.

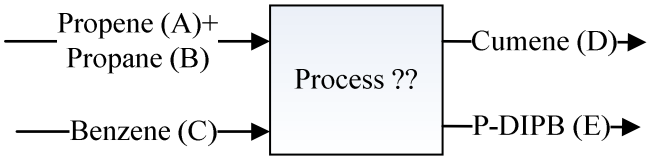
*Table 61: Payback period for membrane unit*

| | **Ibutane-Nbutane** | **Npentane-Ipentane** | |
|---|---|---|---|
| Membrane cost | 2500 | 2500 | Eur / $m^2$ |
| Base Case (Opex) | 258.64 | 712 | Eur /hr |
| Hybrid Case (Opex) | 143.84 | 444 | Eur /hr |
| Membrane area | 109.24 | 1297.6 | $m^2$ |
| Total capex | 273100 | 3244000 | Eur |
| Operational savings | 114.8 | 268 | Eur/hr |
| Payback period | 2378.92 | 12104.48 | hr |
| | 0.27 | 1.38 | Years |

## 5.4 OTHER APPLICATION EXAMPLES:

The developed methodogy was also tested to many other industrially important applications. Table 62 illutrates main results from the application of the method to generate flowsheet alternatives to produce cumene from benzene and propene with propane impurity. In this case study 125 process-groups are initialized. The initialized process-groups are combined to generate 240 feasible flowsheet alternatives for production of cumene. The final design, which is selected with respect to minimum energy consumption, is given in the Figure 73. This is also the design which was suggested by Lubyen for producing cumene from benzene and propene. In another case study, the method is applied to find alternatives to generate biodesiel from lauric acid and methanol. The reaction mechanism for this process is taken from Kiss (Kiss 2011) . A total of 89 process-groups are selected and initialized, these are combined to generate 540 alternatives. Table 63 gives the main results from biodesiel case study. The final design selected for producing biodesiel is given by the Figure 74. For complete list of generated alternatives for both the case studies, refer Table I1 and I2 from Appendix I.

*Table 62: Application method for production of Cumene*

| | |
|---|---|
| **Problem definition :**<br>Production of cumene and p-diisopropylbenzene from benzene and propene (propane impurity) |  |
| **Reaction set:** | Propene + Benzene → Cumene<br>Propene + Cumene → Diisopropylbenzene |
| **Process-groups selected:**<br>Process-groups based on separation techniques : **20**<br><br>Process-groups initialized with different combinations: **125** | (gaAB/C),(gaAB/D), (flAB/E), (gaC/D), (pvC/E), (crD/E), (flAB/C), (flAB/D), (dlAB/E), (crC/D), (pvC/E), (laD/E), (dlAB/C), (dlAB/D), (pvC/D), (laC/D), (dlC/D), (dlC/E), (laD/E), (dlD/E)<br><br>Inlet PG's=2 ; Outlet PG's=2 ; Reactor PG's= 1 Separation PG's= 120 |
| **Flowsheets generated:**<br><br>**Final flowsheet selected:** | Number of flowsheets combinations possible : **280840**<br>Feasible flowsheets (with connectivity rules): **240**<br><br>(iC)[(iAB)](reABC/ABCDE)<1<2(flEDC/AB)1(dlED/C)2(dlE/D) |

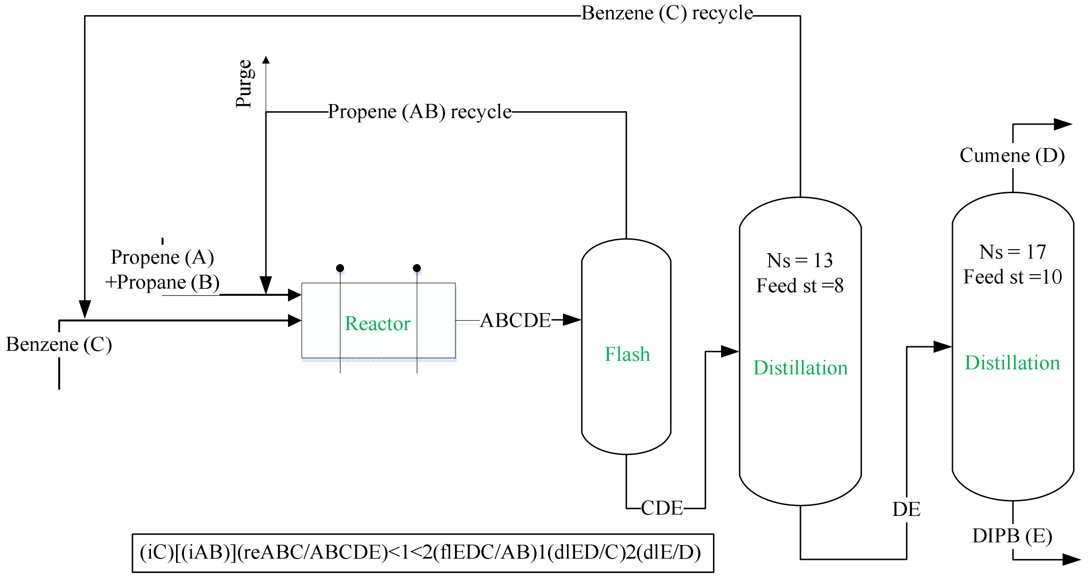
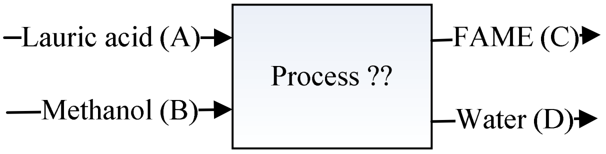


*Figure 73: Final selected design for production of cumene from benzene and propene*

*Table 63: Application method for production of Biodeisel*

| | |
|---|---|
| **Problem definition :**<br>Production of biodiesel (FAME) from methanol and lauric acid |  |
| **Reaction set:** | Lauric Acid + Methanol ⇔ Water + FAME |
| **Process-groups selected:**<br>Process-groups based on separation techniques : **25** | (gaA/B), (pvA/C), (gaA/D), (crB/C), (gaB/D), (lmC/D), (crA/B), (lmA/B), (pvA/B), (laA/B), (dlA/B), (flA/C), (dlA/C), (lmA/D), (pvA/D), (laA/D), (dlA/D), (lmB/C), (pvB/C), (laB/C), (flB/C), (dlB/C), (crB/D), (lmB/D), (pvB/D), (pvB/D), (dlB/D), (pvC/D), (laC/D), (flC/D), (dlC/D) |
| Process-groups initialized with different combinations: **89** | Inlet PG's=2 ; Outlet PG's=2 ; Reactor PG's= 1 Separation PG's= 84 |
| **Flowsheets generated:** | Number of flowsheets combinations possible : **95284**<br>Feasible flowsheets (with connectivity rules): **502** |
| **Final flowsheet selected:** | (iB)[(iA)](reAB/ABCD)<1<2(dlBD/AC)[(dlB/D)1](dlA/C) 2 |

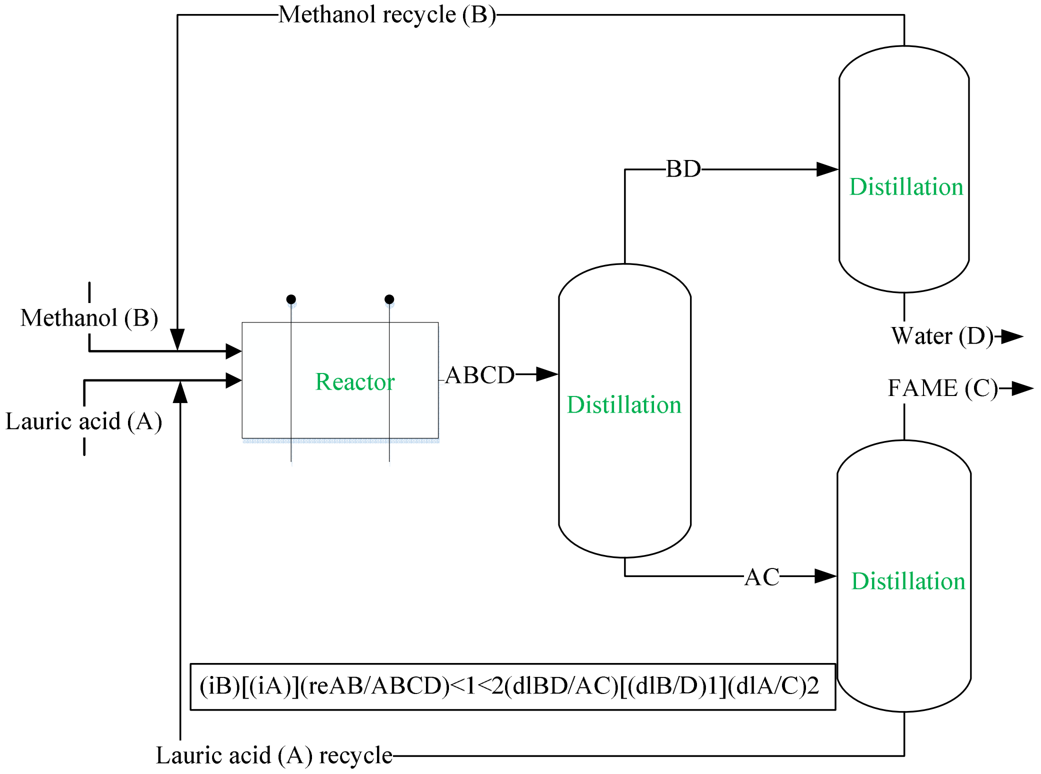


*Figure 74: Final selected design for production of biodiesel from methanol and lauric-acid*

Table 64 gives the information of other examples, which are solved using CAMD methodology for process flowsheets along with references for the results.

*Table 64: Other problems solved by this methodology*

| Process | Raw materials | Alternatives generated | References |
|---|---|---|---|
| Production of Ibuprofen | 4-Isobutyl Phenyl Ethanol | 14 | Papadakis et al. (2016), Papadakis (2016) |
| Production of L-2-aminobutyric acid | 2-oxobutyric acid , benzylamine | 16 | Papadakis et al. (2016) |
| Production of Isobutene | Methyl tert Butyl Ether | 12 | Bommareddy (2014) |
| Production of Succinic Acid | Lignocellulose | 67 | Merlin (2010) |
| Production of Diethyl Succinate | Succinic acid , Ethanol | 40 | Merlin (2010) |

# 6

# CONCLUSIONS AND FUTURE WORK

## 6.1 ACHIEVEMENTS

In this work, the main achievement is the development of a computer-aided method and its prototype to systematically solve the complex process synthesis and design problem, which facilitates more efficient and innovative solutions. The developed method differs significantly from conventional synthesis-design methods as it is not iterative nor is it based solely on mathematical optimization techniques to synthesize an optimal solution. It is a hybrid method based on decomposition based approach where in the complexity of the synthesis problem is decomposed into a set of sub-problems and solved sequentially.

Since the process alternatives are generated by combining the process groups and do not require resolution of the heat and mass balance at each synthesis step, numerous feasible process alternatives can be quickly generated for a given synthesis problem. Unfortunately, any enumeration technique suffers from combinatorial problems as the number of candidate constituents increases. Thus there is a need for fast, reliable and systematic screening methods capable of identifying and ranking the generated process alternatives. In this work, a combinatorial algorithm constituting connectivity and logical decision rules is used to identify the structural feasibility of the process alternatives and generate only feasible solutions. Apart from generating only feasible alternatives, the performance of the generated flowsheet alternatives is quickly tested through flowsheet property models which are estimated from previously regressed contributions of the process-groups involved in the process alternative. These flowsheet property models are truly predictive and component independent, in the sense that it can be applied to any component system as long as the property matches. In the developed method apart from energy consumption analysis, life cycle analysis in the form of evaluating environmental impact and sustainability analysis of process alternatives is carried out in the early stages of the process development to ensure the generated solution is not only an energy optimal solution but also sustainable/green solution. The successful application of this method to benzene production from hydrodealkylation of toluene has demonstrated that synthesis of flowsheets through this group contribution approach quickly generates numerous process alternatives that are truly innovative and that have not been reported in the literature. From this case study it was evident that not only novel but efficient designs can also be generated quickly. For this case study the method was able to generate a total of 64 feasible alternatives. The final optimized design had shown significant improvements in operational profit, LCA and sustainability factors. For the case study involving production of bioethanol, a total of 84 feasible alternatives are generated. And the final selected design is a novel solution to dehydrate ethanol and also requires 35 % less energy than the best published literature design. For the final case study involving separation of alkanes mixture, 184 different flowsheet alternatives were generated. The final solution of this case study has and overall energy savings of 20 % for the entire process and substantial carbon foot print reduction. Finally using the innovative design strategies like simultaneous optimization of process and heat exchanger network, hybrid separations it was proved that the generated alternatives can further be improved in terms of sustainability, economic and life cycle metrics there by giving non-trade of solution for any given synthesis problem.

The main highlights of the developed method are outlined below:

- The method that is applicable for both new synthesis and retrofit problems.
- Decomposition based strategy that does not require rigorous models at every decision step of process synthesis.
- Method that can handle the problems and complexities of enumeration techniques.
- Method that translates the process topology of the generated alternatives in the form an ASCII string for efficient data storage and transfer.
- Modularity and flexibility of the developed method to handle changes or extensions to the method very easily.
- The concept of group contribution based flowsheet property models to evaluate the process alternatives.
- Method that uses concepts of driving force (DF) and attainable region (AR) to generate near optimal design.
- Method that uses comprehensive analysis, consisting of, economic, life cycle and sustainability analyses to aid in generation of green solutions.
- Method that can generate hybrid and integrated solutions using innovative design strategies.
- The method that can easily be transformed to a full fledged process synthesis-design tool that can generate the designs very quickly and efficiently.

## 6.2 FUTURE WORK

1. **Method to include process intensification**: The current method can be extended to include process intensification where in the generated alternative is further innovated through use of intensified unit operations. One of the best ways to truly innovate the design is to investigate alternatives at phenomena scale. In performing intensification at the phenomena scale, not only is the search space of unit operations expanded to include hybrid/intensified unit operations but, also the opportunity to innovate is provided (Lutze et al. 2013; Babi et al. 2015), that is, the generation of novel hybrid/intensified unit operations.

2. **Extension of the method to handle multiple products:** All the case studies tested so far has fixed raw material and products and different process configurations are generated and ranked based on the performance criteria. But the developed method has the capability to generate and evaluate different alternatives where in only the raw material is fixed and synthesis problem is to find the optimal product and processing route. For example, problems involving biorefineries where one has to find the best value added chemical that can be produced from a particular biomass.

3. **Extension of the method to handle multiple raw materials & multiple products:** This problem would be an extension to the one discussed above, wherein given different raw materials and different products that can be produced from each of the raw materials. The method should be able to generate the superstructure of all the alternatives and should be able to find best raw material / product and its optimal processing route.

4. **Expansion of process-groups database and flowsheet property models:** The method strength lies in its capability of generating the alternatives using process-groups and benchmarking them using property models. So process-groups representing new unit operations should developed and added to the existing database to expand the search space of alternatives.

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# ABBREVIATIONS AND NOMENCLATURE

## *Abbreviations*

AR- Attainable Region
Atm- Atmosphere
CAD- Component Assignment Diagram
CAM- Component Assignment Matrix
CAMD- Computer-Aided Molecular Design
CO2 eq- Carbon Dioxide Equivalent
CP- Closed Path
CSTR- Continuous stirred-tank reactor
DF- Driving Force
EWC- Energy to Waste Cost
GWP-Global Warming Potential
HDA- Hydrodealkylation of Toluene
hr- Hour
ICAS- Integrated Computer Aided System
K- Kelvin
L- Liquid
LCA- Life Cycle Analysis
Lit- Liters
LP- Linear Programming
Max- Maximization
Min- Minimization
MINLP- Mixed Integer Nonlinear Programming
MVA- Material Value Added
NC- Number of component in a process group
NG- Number of Process-groups
NLP- Nonlinear Programming
OA- Outer Approximation
OP- Open Path
PFR- Plug Flow Reactor
PG- Process-group
ProPred- Property Prediction

Sec- Seconds

SFILE- Simplified Flowsheet Input Line Entry System

SST- Separation Specification Table

TVA- Total Value Added

V- Vapor

VL- Vapor-Liquid

VV- Vapor-vapor

Yr- Year

## Nomeclature

**A**- Attainable region

A, B, C, - Component identities

$DF_{iMax}$- Maximum driving force available for component i

$Dx_i$- Liquid mole fraction for component i at highest driving force

$E_x$- Energy consumption index

f(P)- Flowsheet property function

HRAT- Heat Recovery Approach Temperature

Nf- Feed stage

$N_{ideal}$- Number of ideal stages

$RR_{min}$- Minimum reflux ratio

X - Design/optimization variable

$x_i$ Liquid mole fraction for component i

$X_{LK,btm}$- Mole fraction of light key in bottoms

$X_{LK,Dist}$- Mole fraction of light key in distillate

Y - Decision integer variables

$y_i$ Vapor mole fraction for component i

z - Set of thermodynamic variables

## Greek Symbols

$\alpha$- Economic Analysis results

$\beta$- Sustainability Analysis results

$\gamma$- LCA Analysis results

$\Delta$Hrxn - Heat of Reaction

$\tau$- Residence time

# APPENDIX A

Pre-calculated values of distillation design data based on driving force approach from Bek Pedersen (Bek-Pedersen 2002).

*Table A.1: Distillation design parameters reflux ratio, minimum reflux ratio, number of stages, product purities, and driving force*

| $F_{DImax}$ | $X_{LK,Dist}$ | $X_{LK, btm}$ | $RR_{min}$ | $RR_{min}C$ | $N_{ideal}$ |
|---|---|---|---|---|---|
| **0.045** | 0.995 | 0.005 | 9.89 | 14.83 | 96 |
| | 0.98 | 0.02 | 9.56 | 14.36 | 71 |
| | 0.95 | 0.05 | 8.9 | 13.35 | 54 |
| | 0.9 | 0.1 | 8.22 | 12.33 | 41 |
| | | | | | |
| **0.065** | 0.995 | 0.005 | 7.33 | 11.00 | 67 |
| | 0.98 | 0.02 | 7.1 | 10.65 | 50 |
| | 0.95 | 0.05 | 6.64 | 9.96 | 38 |
| | 0.9 | 0.1 | 5.72 | 8.58 | 29 |
| | | | | | |
| **0.101** | 0.995 | 0.005 | 4.5 | 6.75 | 44 |
| | 0.98 | 0.02 | 4.35 | 6.53 | 33 |
| | 0.95 | 0.05 | 4.05 | 6.08 | 25 |
| | 0.9 | 0.1 | 3.56 | 5.34 | 19 |
| | | | | | |
| **0.146** | 0.995 | 0.005 | 2.92 | 4.38 | 31 |
| | 0.98 | 0.02 | 2.84 | 4.26 | 23 |
| | 0.95 | 0.05 | 2.63 | 3.95 | 18 |
| | 0.9 | 0.1 | 2.29 | 3.44 | 14 |
| | | | | | |
| **0.172** | 0.995 | 0.005 | 2.35 | 3.53 | 27 |
| | 0.98 | 0.02 | 2.26 | 3.39 | 20 |
| | 0.95 | 0.05 | 2.09 | 3.14 | 15 |
| | 0.9 | 0.1 | 1.8 | 2.70 | 12 |
| | | | | | |
| **0.195** | 0.995 | 0.005 | 2.06 | 3.09 | 24 |
| | 0.98 | 0.02 | 1.89 | 2.835 | 18 |
| | 0.95 | 0.05 | 1.82 | 2.73 | 14 |
| | 0.9 | 0.1 | 1.57 | 2.355 | 11 |
| | | | | | |
| **0.225** | 0.995 | 0.005 | 1.73 | 2.595 | 21 |
| | 0.98 | 0.02 | 1.67 | 2.505 | 16 |
| | 0.95 | 0.05 | 1.53 | 2.295 | 12 |
| | 0.9 | 0.1 | 1.37 | 2.055 | 9 |

| | | | | | |
|---|---|---|---|---|---|
| **0.268** | 0.995 | 0.005 | 1.37 | 2.06 | 18 |
| | 0.98 | 0.02 | 1.31 | 1.97 | 13 |
| | 0.95 | 0.05 | 1.2 | 1.8 | 10 |
| | 0.9 | 0.1 | 1.02 | 1.52 | 8 |
| | | | | | |
| **0.382** | 0.995 | 0.005 | 0.82 | 1.23 | 13 |
| | 0.98 | 0.02 | 0.78 | 1.17 | 10 |
| | 0.95 | 0.05 | 0.7 | 1.05 | 8 |
| | 0.9 | 0.1 | 0.57 | 0.86 | 6 |
| | | | | | |
| **0.478** | 0.995 | 0.005 | 0.54 | 0.81 | 10 |
| | 0.98 | 0.02 | 0.51 | 0.76 | 8 |
| | 0.95 | 0.05 | 0.44 | 0.67 | 6 |
| | 0.9 | 0.1 | 0.34 | 0.51 | 5 |

# APPENDIX B

Knowledge base for hybrid separations synthesis-design method to select $Q_{intermediate}$ and $Q_{target}$ to calculate $Q_{savings}$

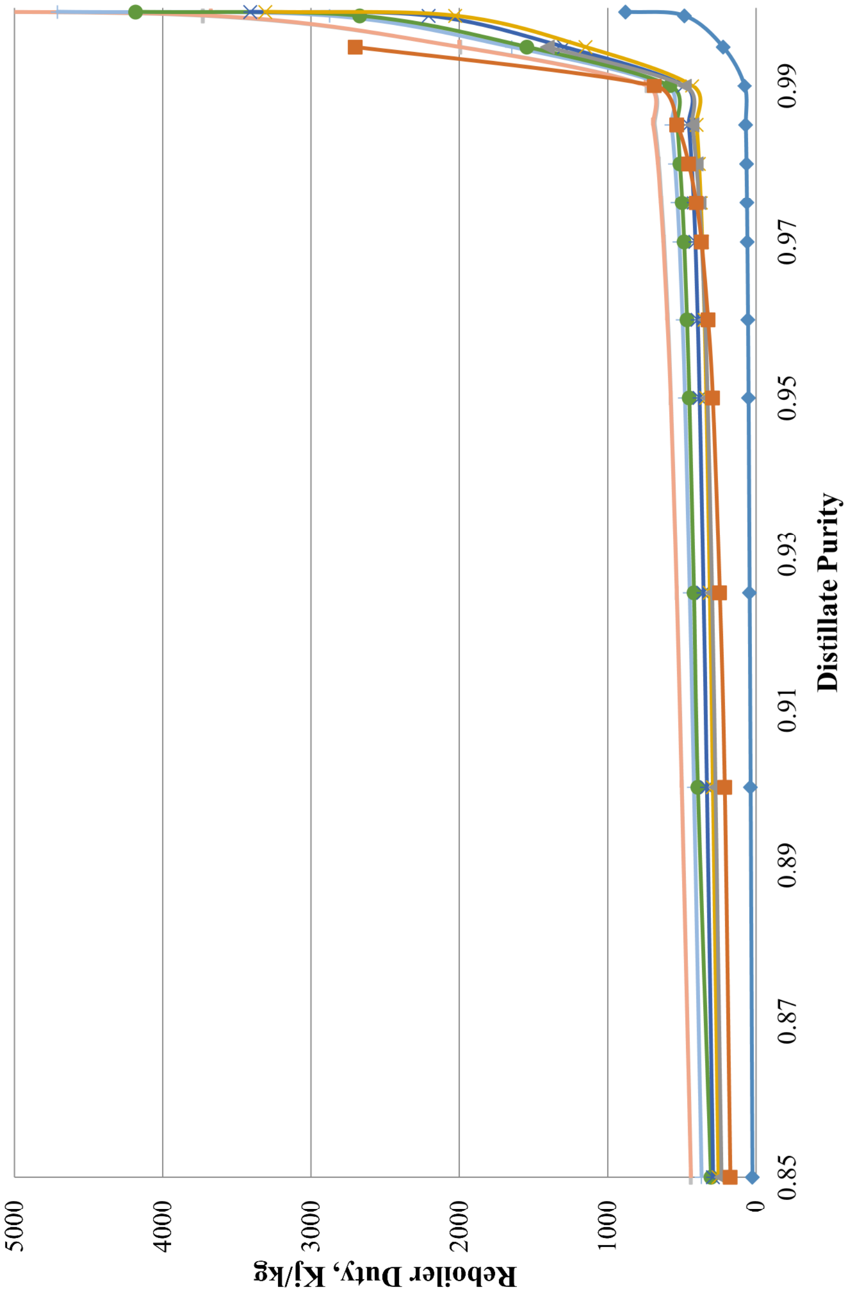

*Figure B.2: Distillate purity vs reboiler duty of Alkanes-Alkenes*

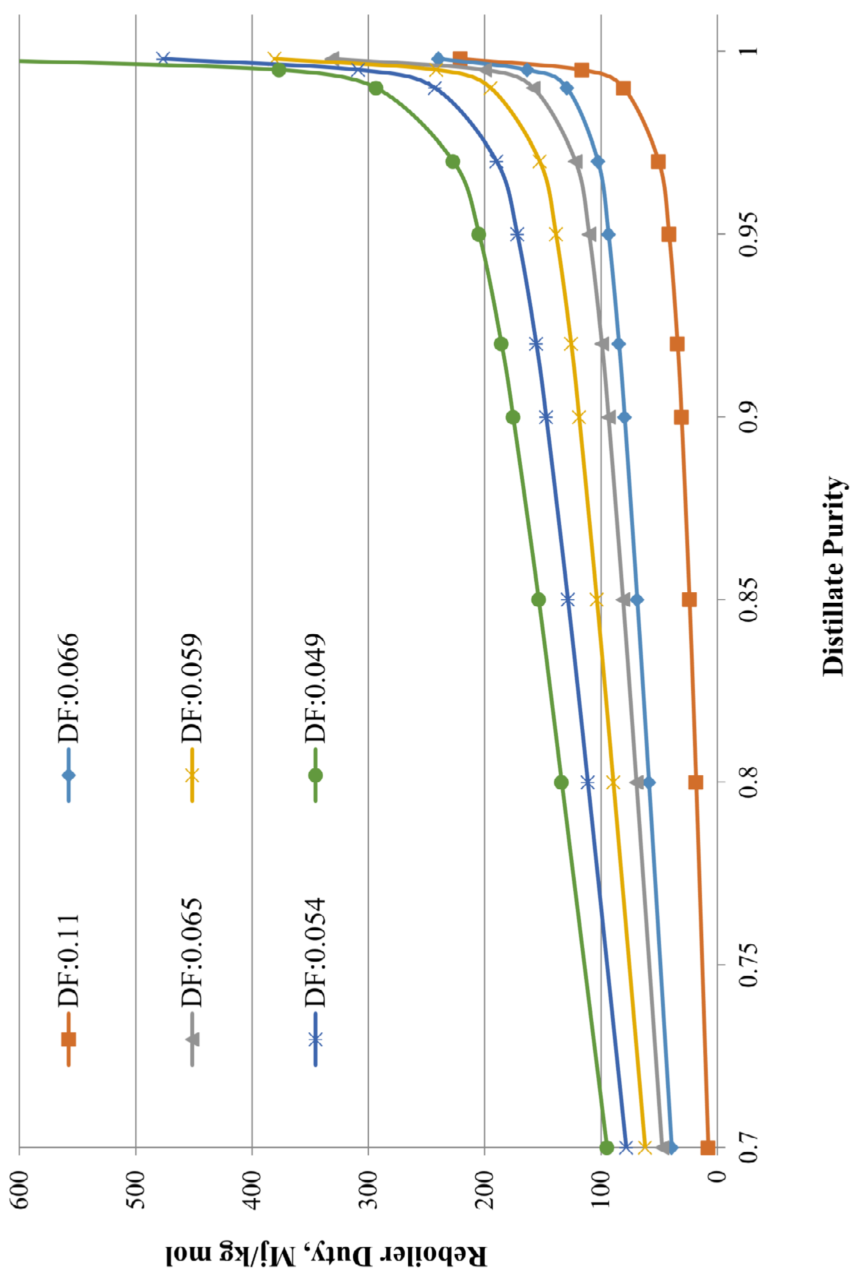

*Figure B.1: Distillate purity vs reboiler duty of Alkanes*

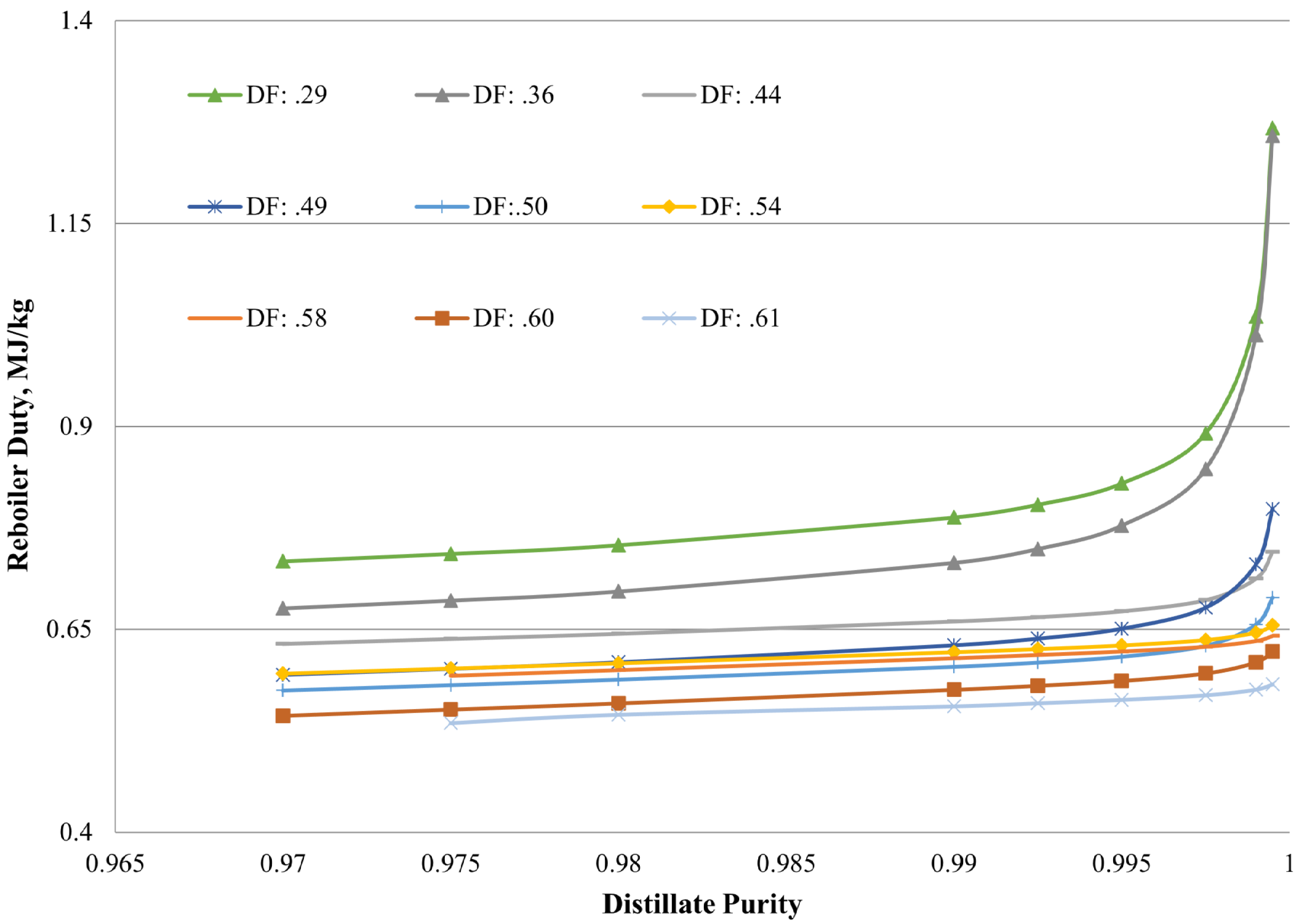

*Figure B.3: Distillate purity vs reboiler duty of Alcohols*

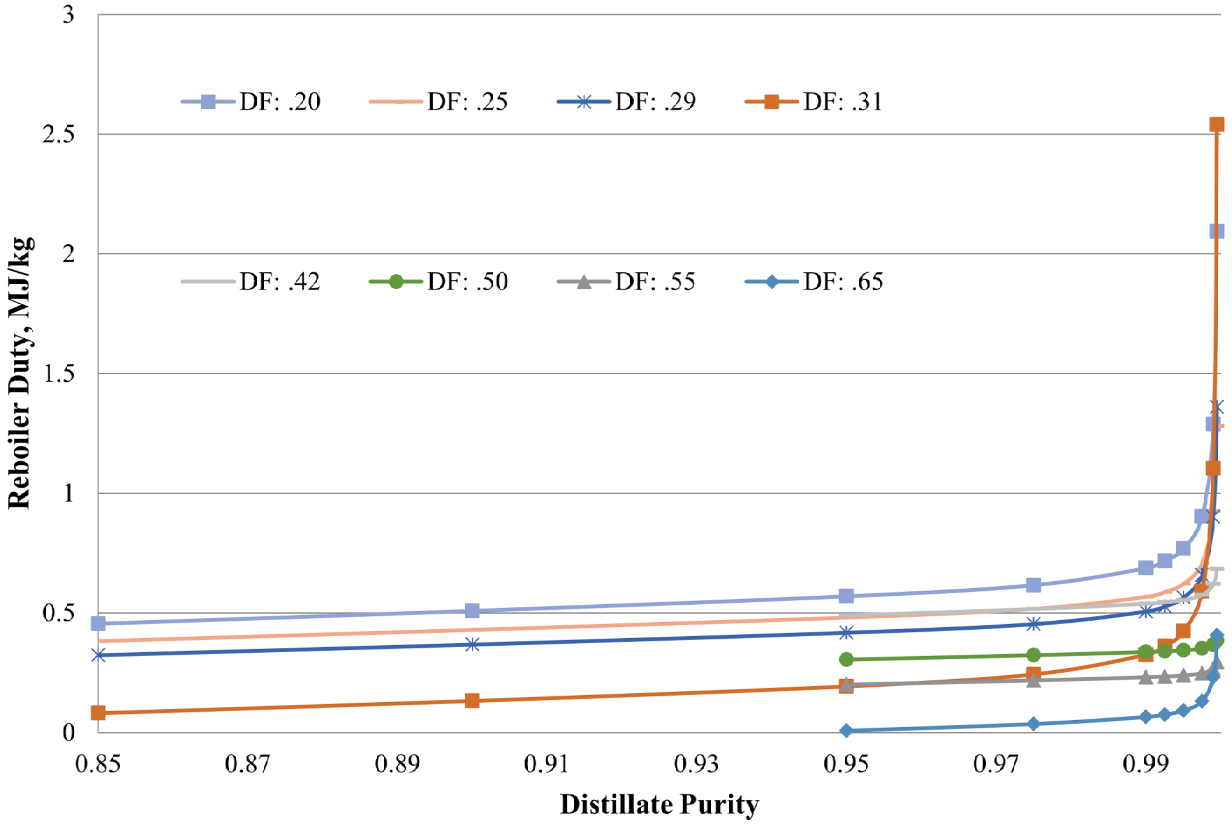

*Figure B.4: Distillate purity vs reboiler duty of Alkynes*

# APPENDIX C

In this section, a detailed description of different process-groups is presented. An overview of each process group is given together with its main characteristics such as property dependence (the physical/chemical/structural property associated with the separation technique represented by the corresponding process group is given); representation procedure (how the process group is set up to be used in a synthesis problem); connectivity rules (the connectivity rules and specifications inherent to the process-group are described); and flowsheet property model parameters.

## C1. Distillation Process-Group:

Distillation process-group represents simple distillation unit operation. This process group can be used to represent both sharp and sloppy separations. The overview of the distillation process-group is given in Table C.1.1.

*Table C.1.1: Distillation process-group overview*

| | |
|---|---|
| **Name** | Distillation PG |
| **Specific properties** | Driving force, Relative volatility |
| **Unit Operations** | Distillation Column |
| **SFLIES notation** | (dlA/B),(dlAB/C) |

**C1.1. Property dependence:** Distillation process-group can be used to represent any separation task as long the following properties are satisfied.

1. No azeotropes must be present between the light and heavy key compounds.
2. The maximum driving force between light and heavy key components must be within the driving force range of the simple distillation process-group (< 0.7).
3. Relative volatilites are with in the range of the distillation process-group

**C1.2. Connectivity rules and Flowsheet property model parameters:**

Distillation process group has one process inlet and two outlets. The inlet connection must contain the exact same components that the ones set during the initialization. All the components present in the outlet connections should be present in the inlet connections. The temperature of the inlet connection depends on the previous connecting process-group, and the bottoms outlet connection is set at bubble point temperature. The distillate connection is set to be bubble point connection for all the compounds except for streams containing non-comdensable gases where the temperature is inilitized as dew point. Produt recoveries and purities are set based on the driving force available for the separation task.

1. DF (0 to 0.15), the product recoveries & purities are set as 99 %.

2. DF (0.15 to 0.35), the product recoveries & purities are set as 99.5 %.

3. DF (> 0.35), the product recoveries & purities are set as 99.8 %.

### C1.3. Regression of the energy index model parameters for distillation process-groups:

Regression of parameters for energy index flowsheet property model is based on rigorous simulation data. Each column in the rigorous simulation has been simulated using standard set of data as given in Table C1.2.

*Table C1.2: Standard setup for rigorous simulation*

| | |
|---|---|
| **Number of stages** | 50 |
| **Minimum recovery of key components** | 99.5% |
| **Minimum purity of a pure key** | 99.5% |
| **Molar flowrate in the inlet** | 1 kmol/hr |
| **Conditions of the inlet** | STP |

The feed plate location is initialized using the driving force method and optimized with the PRO/II optimizer to minimize the total duties of the column. The regressed parameters of the distillation process groups depending on the number of components, the maximum driving force between the key components, the number of components in the overhead products and the relative volatility range of the components.

*Table C1.3: Contributions for distillation process-group energy index model*

| Group | id | NCtotal | NCtop | FDi\|max | ak |
|---|---|---|---|---|---|
| dist-1 | 2 | 1 | 0.157 | 0.01173 | 13.625 |
| dist-2 | 2 | 1 | 0.0664 | 0.04027 | 9.2514 |
| dist-3 | 2 | 1 | 0.1092 | 0.01845 | 10.313 |
| dist-4 | 2 | 1 | 0.0632 | 0.09744 | 7.5854 |
| dist-5 | 2 | 1 | 0.0168 | 6.33727 | 7.0563 |
| dist-6 | 3 | 1 | 0.157 | 0.01016 | 9.2514 |
| dist-7 | 3 | 2 | 0.0664 | 0.06629 | 9.2514 |
| dist-8 | 3 | 1 | 0.0664 | 0.08074 | 10.313 |
| dist-9 | 3 | 2 | 0.1092 | 0.0131 | 10.313 |
| dist-10 | 3 | 1 | 0.1092 | 0.01476 | 7.5854 |
| dist-11 | 3 | 2 | 0.0632 | 0.5262 | 7.5854 |
| dist-12 | 3 | 1 | 0.0632 | 23.71149 | 7.0563 |
| dist-13 | 3 | 2 | 0.0168 | 5.98355 | 7.0563 |
| dist-14 | 3 | 1 | 0.0636 | 0.86774 | 4.0472 |
| dist-15 | 4 | 1 | 0.157 | 0.00808 | 10.313 |
| dist-16 | 4 | 2 | 0.0664 | 0.05101 | 10.313 |
| dist-17 | 4 | 3 | 0.1092 | 0.00911 | 10.313 |
| dist-18 | 4 | 1 | 0.0664 | 0.06426 | 7.5854 |
| dist-19 | 4 | 2 | 0.1092 | 0.01113 | 7.5854 |
| dist-20 | 4 | 3 | 0.0632 | 0.30529 | 7.5854 |
| dist-21 | 4 | 1 | 0.1092 | 0.01278 | 7.0563 |

| | | | | | |
|---|---|---|---|---|---|
| dist-22 | 4 | 2 | 0.0632 | 1.03656 | 7.0563 |
| dist-23 | 4 | 3 | 0.0168 | 5.41363 | 7.0563 |
| dist-24 | 4 | 1 | 0.0168 | 5.97814 | 4.0472 |
| dist-25 | 4 | 2 | 0.0636 | 0.07139 | 4.0472 |
| dist-26 | 5 | 1 | 0.157 | 0.01406 | 7.5854 |
| dist-27 | 5 | 2 | 0.0664 | 0.04336 | 7.5854 |
| dist-28 | 5 | 3 | 0.1092 | 0.00809 | 7.5854 |
| dist-29 | 5 | 4 | 0.0632 | 0.19277 | 7.5854 |
| dist-30 | 5 | 1 | 0.0664 | 0.02434 | 7.0563 |
| dist-31 | 5 | 2 | 0.1092 | 0.00992 | 7.0563 |
| dist-32 | 5 | 3 | 0.0632 | 0.52071 | 7.0563 |
| dist-33 | 5 | 4 | 0.0168 | 5.11638 | 7.0563 |
| dist-34 | 5 | 1 | 0.0632 | 0.12088 | 4.0472 |
| dist-35 | 5 | 2 | 0.0168 | 5.68497 | 4.0472 |
| dist-36 | 5 | 3 | 0.0636 | 0.05739 | 4.0472 |
| dist-37 | 6 | 1 | 0.157 | 0.01262 | 7.0563 |
| dist-38 | 6 | 2 | 0.0664 | 0.01754 | 7.0563 |
| dist-39 | 6 | 3 | 0.1092 | 0.0083 | 7.0563 |
| dist-40 | 6 | 4 | 0.0632 | 0.02942 | 7.0563 |
| dist-41 | 6 | 5 | 0.0168 | 4.53667 | 7.0563 |
| dist-42 | 6 | 1 | 0.1092 | 0.00896 | 4.0472 |
| dist-43 | 6 | 2 | 0.0632 | 0.07976 | 4.0472 |
| dist-44 | 6 | 3 | 0.0168 | 5.16771 | 4.0472 |
| dist-45 | 6 | 4 | 0.0636 | 0.04244 | 4.0472 |
| dist-46 | 7 | 1 | 0.0664 | 0.01506 | 4.0472 |
| dist-47 | 7 | 2 | 0.1092 | 0.00823 | 4.0472 |
| dist-48 | 7 | 3 | 0.0632 | 0.06012 | 4.0472 |
| dist-49 | 7 | 4 | 0.0168 | 4.8943 | 4.0472 |
| dist-50 | 7 | 5 | 0.0636 | 0.03375 | 4.0472 |
| dist-51 | 8 | 1 | 0.157 | 0.01022 | 4.0472 |
| dist-52 | 8 | 2 | 0.0664 | 0.01144 | 4.0472 |
| dist-53 | 8 | 3 | 0.1092 | 0.00714 | 4.0472 |
| dist-54 | 8 | 4 | 0.0632 | 0.01527 | 4.0472 |
| dist-55 | 8 | 5 | 0.0168 | 4.33034 | 4.0472 |
| dist-56 | 8 | 6 | 0.0636 | 0.02561 | 4.0472 |
| dist-57 | 2 | 1 | 0.2199 | 0.01474 | 1.5479 |
| dist-58 | 3 | 2 | 0.2199 | 0.00965 | 1.5479 |
| dist-59 | 3 | 1 | 0.2199 | 0.00696 | 0.028517 |

| | | | | | |
|---|---|---|---|---|---|
| dist-60 | 4 | 3 | 0.2199 | 0.00712 | 1.5479 |
| dist-61 | 4 | 2 | 0.2199 | 0.00516 | 0.028517 |
| dist-62 | 5 | 3 | 0.2199 | 0.00409 | 0.028517 |
| dist-63 | 5 | 4 | 0.7065 | 0.02241 | 0.028517 |

## C2. Crystallization Process-Group:

Crystallization process-group represents simple melt crystallization unit operation. The overview of the crystallization process-group is given in Table C2.1.

*Table C2.1: Crystallization process-group overview*

| **Name** | Crystallization PG |
|---|---|
| **Specific properties** | Melting Point |
| **Unit Operations** | Crystallization |
| **SFLIES notation** | (czA/B),(czAB/C) |

**C2.1. Property dependence:** Crystallization process-group can be used to represent any separation task as long the following properties are satisfied.

1. The binary ratio of melting point for the key pair should be > 1.20

**C2.2. Connectivity rules and Flowsheet property model parameters:**
Crystallization process group has one process inlet and two outlets. The inlet connection must contain the exact same components that the ones set during the initialization. All the components present in the outlet connections should be present in the inlet connections. The temperature of the inlet connection depends on the previous connecting process-group. The outlet temperatures are set based on the solid-liquid equilibrium curve of the binary pair. Produt recoveries for this process-group are set entirely based on the SLE curve and presence of any eutectic points which are caluculated in mixture analysis step. The purity of this process-group is set to be 99.8%.

## C3. Liquid Membrane Process-Group:

Liquid membrane process-group represents simple membrane unit operation where the process conditions are below the boiling point of the mixture or where the separation takes place in liquid phase. The overview of the liquid membrane process-group is given in Table C3.1.

*Table C3.1: Liquid membrane process-group overview*

| **Name** | Liquid membrane PG |
|---|---|
| **Specific properties** | Radius of Gyration, Solubility Parameter and Molar volume |
| **Unit Operations** | Membrane unit |
| **SFLIES notation** | (lmA/B),(lmB/C) |

**C3.1. Property dependence:** Liquid membrane process-group can be used to represent any separation task as long the following properties are satisfied.

1. The binary ratio of radius of gyration point for the key pair should be > 1.03
2. The binary ratio of molar volume for the key pair should be > 1.08
3. The binary ratio of solubility parameter for the key pair should be > 1.25

### C3.2. Connectivity rules and Flowsheet property model parameters:

Liquid membrane process group has one process inlet and two outlets. The inlet connection must contain the exact same components that the ones set during the initialization. All the components present in the outlet connections should be present in the inlet connections. The temperature of the inlet connection depends on the previous connecting process-group. Product recovery and purity by default are kept at 99% for this process-group. If a membrane with high selectivity (>500) is known of the sepration task the product purity is set to 99.5%,

### C4. Gas Membrane Process-Group:

Gas membrane process-group represents simple membrane unit operation where the process conditions are above the boiling point of the mixture or where the separation takes place in gas phase. The overview of the gas membrane process-group is given in Table C4.1.

*Table C4.1: Gas membrane process-group overview*

| | |
|---|---|
| **Name** | Gas membrane PG |
| **Specific properties** | Van der Waals volume and Critical temperature |
| **Unit Operations** | Membrane unit |
| **SFLIES notation** | (gmA/B),(gmB/C) |

**C4.1. Property dependence:** Gas membrane process-group can be used to represent any separation task as long the following properties are satisfied.

1. The binary ratio of Van der Waals volume for the key pair should be > 1.07
2. The binary ratio of critical temperature for the key pair should be > 1.1

### C4.2. Connectivity rules and Flowsheet property model parameters:

Gas membrane process group has one process inlet and two outlets. The inlet connection must contain the exact same components that the ones set during the initialization. All the components present in the outlet connections should be present in the inlet connections. The temperature of the inlet connection depends on the previous connecting process-group. Product recovery and purity by default are kept at 99% for this process-group. If a membrane with high selectivity (>500) is known of the sepration task the product purity is set to 99.5%.

## C5. Molecular Sieve Process-Group:

Molecular Sieve process-group represents simple molecular sieve absorption unit operation where the process conditions are above the boiling point of the mixture or where the separation takes place in gas phase. The overview of the Molecular Sieve membrane process-group is given in Table C5.1.

*Table C5.1: Molecular Sieve process-group overview*

| **Name** | Molecular Sieve PG |
|---|---|
| **Specific properties** | Kinetic diameter and Van der Waals volume |
| **Unit Operations** | Molecular Sieve unit |
| **SFLIES notation** | (msA/B),(msB/C) |

**C5.1. Property dependence:** Molecular Sieve process-group can be used to represent any separation task as long the following properties are satisfied.

1. The binary ratio of Kinetic diameter for the key pair should be > 1.05
2. The binary ratio of Van der Waals volume for the key pair should be > 1.07

**C5.2. Connectivity rules and Flowsheet property model parameters:**
Molecular Sieve process group has one process inlet and two outlets. The inlet connection must contain the exact same components that the ones set during the initialization. All the components present in the outlet connections should be present in the inlet connections. The temperature of the inlet connection depends on the previous connecting process-group. Product recovery for this process-group is set at 99% while the purity factor is set at 99.5%.

## C6. Reactor Process-Group:

Reactor process-group represents both kinetic and simple conversion reactors in the process flowsheet. The overview of the reactor process-group is given in Table C6.1.

*Table C6.1: Reactor process-group overview*

| **Name** | Reactor PG |
|---|---|
| **Specific properties** | Conversion or Kinetics |
| **Unit Operations** | CSTR , PFR |
| **SFLIES notation** | (rxAB/ABCD) |

**C6.1. Property dependence:** The reactor process-group can be used to represent any separation task as long the following properties are satisfied.

1. All the reactants needed for the process group are available in the mixture.
2. All conversion rates/kinetics are known.

**C6.2. Connectivity rules:**
By default reactor process-group has one inlet and one outlet connections. However the inlet connections can be more depending on the recyle connections. The pressure and the temperature of the outlet is set to the operational conditions of the reactor. The outlet contains a mixture of all the reactants, inerts and products.

## C7. Liquid-Liquid Extraction Process-Group:

Liquid-Liquid extraction process group is a cyclic process group which includes extraction column and solvent recovery column. This cyclic process group overall has two process inlets and two outlets. The process inlets refer to feed mixture and solvent while the outlets streams refer to the components. The overview of the liquid-liquid extraction process-group is given in Table C7.1.

*Table C7.1: Liquid-Liquid extraction process-group overview*

| **Name** | Liquid-Liquid extraction process group |
|---|---|
| **Specific properties** | Solvent free driving force, Solubility parameter, Azeotrope and Driving force for recovery column |
| **Unit Operations** | Extraction column and solvent recovery column |
| **SFLIES notation** | (llSAB/SA) (llSAB/SB) |

**C7.1. Property dependence:** Liquid-Liquid extraction process group can be used to represent any separation task as long the following properties are satisfied.

For Extraction column:

1. The solubility parameter ratio between solute and solvent is greater than 1.1 and the solubility parameter ratio between carrier (co solute) and solvent is lower than 1.1
2. 2-Phase formation on addition of solvent (Ternary plot).

For Recovery column:

1. No azeotropes must be present between the light and heavy key compounds.
2. The maximum driving force between light and heavy key components must be within the driving force range of the simple distillation process-group (< 0.7).
3. Relative volatilites are with in the range of the distillation process-group

**C7.2. Connectivity rules and Flowsheet property model parameters:**

Liquid-Liquid extraction process group has one process inlet and two outlets. The temperature of the inlet connection depends on the previous connecting process-group and process operation si considered at STP. Product recovery for this process-group is set at 99% while the purity factor is set at 99.5%. For energy calculation only the solvent recovery column duty is calculated using the driving force of solvent and solute using Energy index flowsheet property model.

## C8. Extractive Distillation Process-Group:

This process-group is also a cyclic process-group which represents a extractive distillation setup tp separate and azeotropic mixture. The process-group consists of two columns, where the first column is the extractive distillation unit where one product is obtained and the second column referes to solvent recovery section. The overview of the extractive distillation process-group is given in Table C8.1.

*Table C8.1 : Extractive Distillation process-group overview*

| **Name** | Extractive Distillation PG |
|---|---|
| **Specific properties** | Conversion or Kinetics |
| **Unit Operations** | Extractive column and solvent recovery column |
| **SFLIES notation** | (edSAB/SB) (edSAB/SA) |

**C8.1. Property dependence:** The extractive distillation process-group can be used to represent any separation task as long the following properties are satisfied.

For Extractive column:

1. The mixture (key components) is an azeotropic mixture.
2. The solvent free maximum driving force between the two key components is within the driving force range of the solvent based separation. This implies the availability of an adequate solvent for the separation of the selected key pair.

For Recovery column:

1. No azeotropes must be present between the light and heavy key compounds.
2. The maximum driving force between light and heavy key components must be within the driving force range of the simple distillation process-group (< 0.7).
3. Relative volatilites are with in the range of the distillation process-group

### C8.2. Connectivity rules and Flowsheet property model parameters:

The extractive distillation process group overall has one inlet two outlets process group. The uptake of solvent is not an inlet of the process group. The temperature of the inlet connection depends on the previous connecting process-group, and the bottoms outlet connection is set at bubble point temperature. The distillate connection is set to be bubble point. Produt recoveries and purities are set based on the driving force available for the separation task in both the columns.

For extractive column: DF plotted on solventfree basis

1. DF (0 to 0.15), the product recoveries & purities are set as 99 %.
2. DF (0.15 to 0.35), the product recoveries & purities are set as 99.5 %.

For recovery column:

1. DF (0 to 0.15), the product recoveries & purities are set as 99 %.
2. DF (0.15 to 0.35), the product recoveries & purities are set as 99.5 %.
3. DF (> 0.35), the product recoveries & purities are set as 99.8 %.

### C8.3. Regression of the energy index model parameters Extractive column:

In this section the procedure to obtain the energy index model parameters of the extractive column is described (Merlin 2010). The regressed model parameters generated are tabulated.

1. Define the separation task related to the process group.
2. Construct the solvent free DF diagram for different solvent loadings (fraction of the feed), either from experimental data or VLE calculations.

3. Perform a set of simulation tasks for different solvent fractions to generate pseudo experimental data with respect to energy consumption. Run simulations to generate energy consumptions for extractive column.
4. For each solvent fraction used in step 3, obtain maximum driving force from the solvent free DF diagram as shown in Figure C8.1.
5. From Equation C8.1 obtain the $a_k$ parameters through the minimization of the energy consumption of the process as shown in the objective function given by Eq. (C8.2).

$$E_x = \sum_{k=1}^{n=NG} Q_k = \sum_{k=1}^{n=NG} \frac{(1+p_k)}{d_{ij}^{k}} * a_k \qquad \text{(C8.1)}$$

$$Fobj = Min \sum_{k=1}^{Np} (E_j^{Exp} - E_j^{Cal})\,\hat{}^{2} \qquad \text{(C8.2)}$$

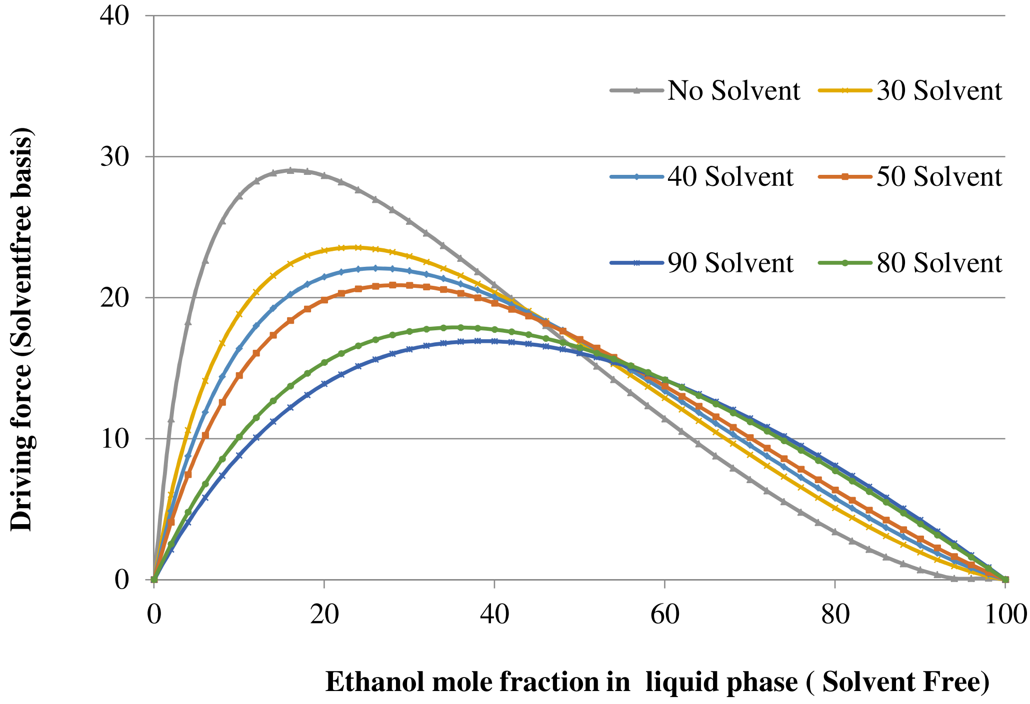

*Figure C8.1: Solvent free DF diagram for Ethanol/water mixture separation with Ethylene-glycol*

Model parameters for Extractive column using water- ethanol feed mixture is given in Table C8.2

*Table C8.2: Model parameters to estimate Energy index for extractive column*

| **Solvent Fraction** | **Maximum driving force ($d^k_{ij}$)** | **$a_k$** |
|---|---|---|
| 0.279204 | 0.41837 | 0.018 |
| 0.29883 | 0.42339 | 0.017 |
| 0.332557 | 0.43182 | 0.017 |
| 0.374181 | 0.44189 | 0.016 |
| 0.399162 | 0.44811 | 0.016 |
| 0.449136 | 0.45997 | 0.016 |
| 0.472813 | 0.46529 | 0.015 |
| 0.499127 | 0.47096 | 0.015 |
| 0.522938 | 0.47568 | 0.015 |

# APPENDIX D

In this section all the process alternatives generated for benzene production from hydrodealkylation of toluene (HDA) process is given in the form of SFILES representation.

*Table D1: SFILES of generated process alternatives.*

| Sno | SFILES |
|---|---|
| 1 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](C/DE)[(oC)](crsE/D)[(oD)2](oE) |
| 2 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](C/DE)[(oC)](D/E)[(oD)2](oE) |
| 3 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](C/DE)[(oC)](msE/D)[(oD)2](oE) |
| 4 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemED/C)[(oC)](crsE/D)[(oD)2](oE) |
| 5 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](C/DE)[(oC)](lmemE/D)[(oD)2](oE) |
| 6 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemED/C)[(oC)](D/E)[(oD)2](oE) |
| 7 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msED/C)[(oC)](crsE/D)[(oD)2](oE) |
| 8 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemED/C)[(oC)](msE/D)[(oD)2](oE) |
| 9 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemED/C)[(oC)](lmemE/D)[(oD)2](oE) |
| 10 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msED/C)[(oC)](D/E)[(oD)]2(oE) |
| 11 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msED/C)[(oC)](msE/D)[(oD)2](oE) |
| 12 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msED/C)[(oC)](lmemE/D)[(oD)2](oE) |
| 13 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsE/CD)[(oE)](C/D)[(oD)2](oC) |
| 14 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](CD/E)[(oE)](C/D)[(oD)2](oC) |
| 15 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsE/CD)[(oE)](lmemD/C)[(oD)2](oC) |
| 16 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsE/CD)[(oE)](msD/C)[(oD)2](oC) |
| 17 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](CD/E)[(oE)](lmemD/C)[(oD)2](oC) |

| | |
|---|---|
| 18 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemE/DC)[(oE)](C/D)[(oD)2](oC) |
| 19 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msE/DC)[(oE)](C/D)[(oD)2](oC) |
| 20 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemE/DC)[(oE)](lmemD/C)[(oD)2](oC) |
| 21 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](CD/E)[(oE)](msD/C)[(oD)2](oC) |
| 22 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msE/DC)[(oE)](msD/C)[(oD)2](oC) |
| 23 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsEC/D)[(oD)2](crsE/C)[(oE)](oC) |
| 24 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemE/DC)[(oE)](msD/C)[(oD)2](oC) |
| 25 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsEC/D)[(oD)2](C/E)[(oE)](oC) |
| 26 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msE/DC)[(oE)](lmemD/C)[(oD)2](oC) |
| 27 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsEC/D)[(oD)2](lmemE/C)[(oE)](oC) |
| 28 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsEC/D)[(oD)2](msE/C)[(oE)](oC) |
| 29 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](crsE/CD)[(oE)](crsC/D)[(oD)2](oC) |
| 30 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](lmemE/DC)[(oE)](crsC/D)[(oD)2](oC) |
| 31 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](CD/E)[(oE)](crsC/D)[(oD)2](oC) |
| 32 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(oAB)1](msE/DC)[(oE)](crsC/D)[(oD)2](oC) |
| 33 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](C/DE)[(oC)](crsE/D)[(oD)2](oE) |
| 34 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](C/DE)[(oC)](D/E)[(oD)2](oE) |
| 35 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](C/DE)[(oC)](msE/D)[(oD)2](oE) |
| 36 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemED/C)[(oC)](crsE/D)[(oD)2](oE) |
| 37 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](C/DE)[(oC)](lmemE/D)[(oD)2](oE) |
| 38 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemED/C)[(o |

| | |
|---|---|
| | C)](D/E)[(oD)2](oE) |
| 39 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msED/C)[(oC)](crsE/D)[(oD)2](oE) |
| 40 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemED/C)[(oC)](msE/D)[(oD)2](oE) |
| 41 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemED/C)[(oC)](lmemE/D)[(oD)2](oE) |
| 42 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msED/C)[(oC)](D/E)[(oD)]2(oE) |
| 43 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msED/C)[(oC)](msE/D)[(oD)2](oE) |
| 44 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msED/C)[(oC)](lmemE/D)[(oD)2](oE) |
| 45 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsE/CD)[(oE)](C/D)[(oD)2](oC) |
| 46 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](CD/E)[(oE)](C/D)[(oD)2](oC) |
| 47 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsE/CD)[(oE)](lmemD/C)[(oD)2](oC) |
| 48 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsE/CD)[(oE)](msD/C)[(oD)2](oC) |
| 49 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](CD/E)[(oE)](lmemD/C)[(oD)2](oC) |
| 50 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemE/DC)[(oE)](C/D)[(oD)2](oC) |
| 51 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msE/DC)[(oE)](C/D)[(oD)2](oC) |
| 52 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemE/DC)[(oE)](lmemD/C)[(oD)2](oC) |
| 53 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](CD/E)[(oE)](msD/C)[(oD)2](oC) |
| 54 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msE/DC)[(oE)](msD/C)[(oD)2](oC) |
| 55 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsEC/D)[(oD)2](crsE/C)[(oE)](oC) |
| 56 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemE/DC)[(oE)](msD/C)[(oD)2](oC) |
| 57 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsEC/D)[(oD)2](C/E)[(oE)](oC) |
| 58 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msE/DC)[(oE)](lmemD/C)[(oD)2](oC) |

| | |
|---|---|
| 59 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsEC/D)[(oD)2](lmemE/C)[(oE)](oC) |
| 60 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsEC/D)[(oD)2](msE/C)[(oE)](oC) |
| 61 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](crsE/CD)[(oE)](crsC/D)[(oD)2](oC) |
| 62 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](lmemE/DC)[(oE)](crsC/D)[(oD)2](oC) |
| 63 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](CD/E)[(oE)](crsC/D)[(oD)2](oC) |
| 64 | (iAB)(rAD/ABCDE)<1<2[(<iD)](AB/CDE)[(gmemA/B)[(oB)](oA)1](msE/DC)[(oE)](crsC/D)[(oD)2](oC) |

# APPENDIX E

In this section all the process alternatives generated for bioethnaol production from lignocellulostic rawmaterial process is given in the form of SFILES representation.

*Table E1: SFILES of generated process alternatives.*

| Design no | SMILES |
|---|---|
| 1 | (dcABCDEF/M)(flAB/CDEF)(pvC/DEF)(oC) |
| 2 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(crC/E)(oC) |
| 3 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(pvC/E)(oC) |
| 4 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(dlC/E)(oC) |
| 5 | (dcABCDEF/M)(flAB/CDEF)(pvD/CEF)(lmC/E)(oC) |
| 6 | (dcABCDEF/M)(flAB/CDEF)(crD/CEF)(crC/E)(oC) |
| 7 | (dcABCDEF/M)(flAB/CDEF)(crD/CEF)pvC/E)(oC) |
| 8 | (dcABCDEF/M)(flAB/CDEF)(crD/CEF)(dlC/E)(oC) |
| 9 | (dcABCDEF/M)(flAB/CDEF)(crD/CEF)(lmC/E)(oC) |
| 10 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(msC/D)(oC) |
| 11 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(pvC/D)(oC) |
| 12 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](pvD/S) |
| 13 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](dlD/S) |
| 14 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](lmD/S) |
| 15 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](pvD/S) |
| 16 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](dlD/S) |
| 17 | (dcABCDEF/M)(flAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](lmD/S) |
| 18 | (dcABCDEF/M)(flAB/CDEF)(llCS/DEF)(pvC/S)(oC) |
| 19 | (dcABCDEF/M)(flAB/CDEF)(llCS/DEF)(dlC/S)(oC) |
| 20 | (dcABCDEF/M)(flAB/CDEF)(llCS/DEF)(lmC/S)(oC) |
| 21 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(msC/D)(oC) |
| 22 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)pvC/D)(oC) |
| 23 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](pvD/S) |
| 24 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](dlD/S) |
| 25 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](lmD/S) |
| 26 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](pvD/S) |
| 27 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](dlD/S) |
| 28 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](lmD/S) |
| 29 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(msC/D)(oC) |
| 30 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)pvC/D)(oC) |
| 31 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](pvD/S) |
| 32 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](dlD/S) |
| 33 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](lmD/S) |
| 34 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](pvD/S) |
| 35 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](dlD/S) |

| | |
|---|---|
| 36 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](lmD/S) |
| 37 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(msC/D)(oC) |
| 38 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)pvC/D)(oC) |
| 39 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](pvD/S) |
| 40 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](dlD/S) |
| 41 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](lmD/S) |
| 42 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](pvD/S) |
| 43 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](dlD/S) |
| 44 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](lmD/S) |
| 45 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCS/D)(pvC/S)(oC) |
| 46 | (dcABCDEF/M)(flAB/CDEF)(llCDS/DEF)(pvCS/D)(dlC/S)(oC) |
| 47 | (dcABCDEF/M)(dlAB/CDEF)(pvC/DEF)(oC) |
| 48 | (dcABCDEF/M)(dlAB/CDEF)(pvD/CEF)(crC/E)(oC) |
| 49 | (dcABCDEF/M)(dlAB/CDEF)(pvD/CEF)pvC/E)(oC) |
| 50 | (dcABCDEF/M)(dlAB/CDEF)(pvD/CEF)(dlC/E)(oC) |
| 51 | (dcABCDEF/M)(dlAB/CDEF)(pvD/CEF)(lmC/E)(oC) |
| 52 | (dcABCDEF/M)(dlAB/CDEF)(crD/CEF)(crC/E)(oC) |
| 53 | (dcABCDEF/M)(dlAB/CDEF)(crD/CEF)pvC/E)(oC) |
| 54 | (dcABCDEF/M)(dlAB/CDEF)(crD/CEF)(dlC/E)(oC) |
| 55 | (dcABCDEF/M)(dlAB/CDEF)(crD/CEF)(lmC/E)(oC) |
| 56 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(msC/D)(oC) |
| 57 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)pvC/D)(oC) |
| 58 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](pvD/S) |
| 59 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](dlD/S) |
| 60 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(azC/SD)[(oC)](lmD/S) |
| 61 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](pvD/S) |
| 62 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](dlD/S) |
| 63 | (dcABCDEF/M)(dlAB/CDEF)(dlCD/DEF)(edC/SD)[(oC)](lmD/S) |
| 64 | (dcABCDEF/M)(dlAB/CDEF)(llCS/DEF)(pvC/S)(oC) |
| 65 | (dcABCDEF/M)(dlAB/CDEF)(llCS/DEF)(dlC/S)(oC) |
| 66 | (dcABCDEF/M)(dlAB/CDEF)(llCS/DEF)(lmC/S)(oC) |
| 67 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(msC/D)(oC) |
| 68 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)pvC/D)(oC) |
| 69 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](pvD/S) |
| 70 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](dlD/S) |
| 71 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(azC/SD)[(oC)](lmD/S) |
| 72 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](pvD/S) |
| 73 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](dlD/S) |
| 74 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(lmCD/S)(edC/SD)[(oC)](lmD/S) |
| 75 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(msC/D)(oC) |
| 76 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)pvC/D)(oC) |
| 77 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](pvD/S) |

| | |
|---|---|
| 78 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](dlD/S) |
| 79 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(azC/SD)[(oC)](lmD/S) |
| 80 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](pvD/S) |
| 81 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](dlD/S) |
| 82 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCD/S)(edC/SD)[(oC)](lmD/S) |
| 83 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(msC/D)(oC) |
| 84 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)pvC/D)(oC) |
| 85 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](pvD/S) |
| 86 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](dlD/S) |
| 87 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(azC/SD)[(oC)](lmD/S) |
| 88 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](pvD/S) |
| 89 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](dlD/S) |
| 90 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(dlCD/S)(edC/SD)[(oC)](lmD/S) |
| 91 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCS/D)(pvC/S)(oC) |
| 92 | (dcABCDEF/M)(dlAB/CDEF)(llCDS/DEF)(pvCS/D)(dlC/S)(oC) |
| | |

# APPENDIX F

In this section all the process alternatives generated for sepraration of Alkanes mixture is given in the form of SFILES representation.

*Table F1: SFILES of generated process alternatives.*

| Design no | SFILES |
|---|---|
| 1 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(gaED/C)(dlE/D) |
| 2 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(pvED/C)(dlE/D) |
| 3 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(laED/C)(dlE/D) |
| 4 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlED/C)(dlE/D) |
| 5 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlE/DC)(gaD/C) |
| 6 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlE/DC)(pvD/C) |
| 7 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlE/DC)(laD/C) |
| 8 | (iABCDE)(mABCDE)(gaEDCB/A)(pvEDC/B)(dlE/DC)(dlD/C) |
| 9 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(gaED/C)(dlE/D) |
| 10 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(pvED/C)(dlE/D) |
| 11 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(laED/C)(dlE/D) |
| 12 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(dlED/C)(dlE/D) |
| 13 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(dlE/DC)(gaD/C) |
| 14 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(dlE/DC)(pvD/C) |
| 15 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(dlE/DC)(laD/C) |
| 16 | (iABCDE)(mABCDE)(gaEDCB/A)(dlEDC/B)(dlE/DC)(dlD/C) |
| 17 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvDC/B)(gaD/C) |
| 18 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvDC/B)(pvD/C) |
| 19 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvDC/B)(laD/C) |
| 20 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvDC/B)(dlD/C) |
| 21 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlDC/B)(gaD/C) |
| 22 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlDC/B)(pvD/C) |
| 23 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlDC/B)(laD/C) |
| 24 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlDC/B)(dlD/C) |
| 25 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(gaD/CB)(pvC/B) |
| 26 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(gaD/CB)(dlC/B) |
| 27 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvD/CB)(pvC/B) |
| 28 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(pvD/CB)(dlC/B) |
| 29 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(laD/CB)(pvC/B) |
| 30 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(laD/CB)(dlC/B) |
| 31 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlD/CB)(pvC/B) |
| 32 | (iABCDE)(mABCDE)(gaEDCB/A)(dlE/DBC)(dlD/CB)(dlC/B) |
| 33 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(gaED/C)(dlE/D) |
| 34 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(pvED/C)(dlE/D) |

| | |
|---|---|
| 35 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(laED/C)(dlE/D) |
| 36 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(dlED/C)(dlE/D) |
| 37 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(dlE/DC)(gaD/C) |
| 38 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(dlE/DC)(pvD/C) |
| 39 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(dlE/DC)(laD/C) |
| 40 | (iABCDE)(mABCDE)(dlEDCB/A)(pvEDC/B)(dlE/DC)(dlD/C) |
| 41 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(gaED/C)(dlE/D) |
| 42 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(pvED/C)(dlE/D) |
| 43 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(laED/C)(dlE/D) |
| 44 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlED/C)(dlE/D) |
| 45 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlE/DC)(gaD/C) |
| 46 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlE/DC)(pvD/C) |
| 47 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlE/DC)(laD/C) |
| 48 | (iABCDE)(mABCDE)(dlEDCB/A)(dlEDC/B)(dlE/DC)(dlD/C) |
| 49 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvDC/B)(gaD/C) |
| 50 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvDC/B)(pvD/C) |
| 51 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvDC/B)(laD/C) |
| 52 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvDC/B)(dlD/C) |
| 53 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlDC/B)(gaD/C) |
| 54 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlDC/B)(pvD/C) |
| 55 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlDC/B)(laD/C) |
| 56 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlDC/B)(dlD/C) |
| 57 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(gaD/CB)(pvC/B) |
| 58 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(gaD/CB)(dlC/B) |
| 59 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvD/CB)(pvC/B) |
| 60 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(pvD/CB)(dlC/B) |
| 61 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(laD/CB)(pvC/B) |
| 62 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(laD/CB)(dlC/B) |
| 63 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlD/CB)(pvC/B) |
| 64 | (iABCDE)(mABCDE)(dlEDCB/A)(dlE/DBC)(dlD/CB)(dlC/B) |
| 65 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvDC/B)(gaD/C) |
| 66 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvDC/B)(pvD/C) |
| 67 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvDC/B)(laD/C) |
| 68 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvDC/B)(dlD/C) |
| 69 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlDC/B)(gaD/C) |
| 70 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlDC/B)(pvD/C) |
| 71 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlDC/B)(laD/C) |
| 72 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlDC/B)(dlD/C) |
| 73 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(gaD/CB)(pvC/B) |
| 74 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(gaD/CB)(dlC/B) |
| 75 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvD/CB)(pvC/B) |
| 76 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(pvD/CB)(dlC/B) |

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|---|---|
| 77 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(laD/CB)(pvC/B) |
| 78 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(laD/CB)(dlC/B) |
| 79 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlD/CB)(pvC/B) |
| 80 | (iABCDE)(mABCDE)(dlE/DABC)(gaDCB/A)(dlD/CB)(dlC/B) |
| 81 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvDC/B)(gaD/C) |
| 82 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvDC/B)(pvD/C) |
| 83 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvDC/B)(laD/C) |
| 84 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvDC/B)(dlD/C) |
| 85 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlDC/B)(gaD/C) |
| 86 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlDC/B)(pvD/C) |
| 87 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlDC/B)(laD/C) |
| 88 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlDC/B)(dlD/C) |
| 89 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(gaD/CB)(pvC/B) |
| 90 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(gaD/CB)(dlC/B) |
| 91 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvD/CB)(pvC/B) |
| 92 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(pvD/CB)(dlC/B) |
| 93 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(laD/CB)(pvC/B) |
| 94 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(laD/CB)(dlC/B) |
| 95 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlD/CB)(pvC/B) |
| 96 | (iABCDE)(mABCDE)(dlE/DABC)(dlDCB/A)(dlD/CB)(dlC/B) |
| 97 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(gaCB/A)(pvC/B) |
| 98 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(gaCB/A)(dlC/B) |
| 99 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(dlCB/A)(pvC/B) |
| 100 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(dlCB/A)(dlC/B) |
| 101 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(dlC/BA)(gaB/A) |
| 102 | (iABCDE)(mABCDE)(dlE/DABC)(gaD/CAB)(dlC/BA)(dlB/A) |
| 103 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(gaCB/A)(pvC/B) |
| 104 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(gaCB/A)(dlC/B) |
| 105 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(dlCB/A)(pvC/B) |
| 106 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(dlCB/A)(dlC/B) |
| 107 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(dlC/BA)(gaB/A) |
| 108 | (iABCDE)(mABCDE)(dlE/DABC)(pvD/CAB)(dlC/BA)(dlB/A) |
| 109 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(gaCB/A)(pvC/B) |
| 110 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(gaCB/A)(dlC/B) |
| 111 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(dlCB/A)(pvC/B) |
| 112 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(dlCB/A)(dlC/B) |
| 113 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(dlC/BA)(gaB/A) |
| 114 | (iABCDE)(mABCDE)(dlE/DABC)(laD/CAB)(dlC/BA)(dlB/A) |
| 115 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(gaCB/A)(pvC/B) |
| 116 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(gaCB/A)(dlC/B) |
| 117 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(dlCB/A)(pvC/B) |
| 118 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(dlCB/A)(dlC/B) |

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|---|---|
| 119 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(dlC/BA)(gaB/A) |
| 120 | (iABCDE)(mABCDE)(dlE/DABC)(dlD/CAB)(dlC/BA)(dlB/A) |
| 121 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](gaED/C)(dlE/D) |
| 122 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](gaED/C)(dlE/D) |
| 123 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](pvED/C)(dlE/D) |
| 124 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](pvED/C)(dlE/D) |
| 125 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](laED/C)(dlE/D) |
| 126 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](laED/C)(dlE/D) |
| 127 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](dlED/C)(dlE/D) |
| 128 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](dlED/C)(dlE/D) |
| 129 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](dlE/DC)(gaD/C) |
| 130 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](dlE/DC)(gaD/C) |
| 131 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](dlE/DC)(pvD/C) |
| 132 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](dlE/DC)(pvD/C) |
| 133 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](dlE/DC)(laD/C) |
| 134 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](dlE/DC)(laD/C) |
| 135 | (iABCDE)(mABCDE)(dlEDC/BA)[(gaB/A)](dlE/DC)(dlD/C) |
| 136 | (iABCDE)(mABCDE)(dlEDC/BA)[(dlB/A)](dlE/DC)(dlD/C) |
| 137 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](gaCB/A)(pvC/B) |
| 138 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](gaCB/A)(dlC/B) |
| 139 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](dlCB/A)(pvC/B) |
| 140 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](dlCB/A)(dlC/B) |
| 141 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](dlC/BA)(gaB/A) |
| 142 | (iABCDE)(mABCDE)(gaED/CAB)[(dlE/D)](dlC/BA)(dlB/A) |
| 143 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](gaCB/A)(pvC/B) |
| 144 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](gaCB/A)(dlC/B) |
| 145 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](dlCB/A)(pvC/B) |
| 146 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](dlCB/A)(dlC/B) |
| 147 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](dlC/BA)(gaB/A) |
| 148 | (iABCDE)(mABCDE)(pvED/CAB)[(dlE/D)](dlC/BA)(dlB/A) |
| 149 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](gaCB/A)(pvC/B) |
| 150 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](gaCB/A)(dlC/B) |
| 151 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](dlCB/A)(pvC/B) |
| 152 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](dlCB/A)(dlC/B) |
| 153 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](dlC/BA)(gaB/A) |
| 154 | (iABCDE)(mABCDE)(laED/CAB)[(dlE/D)](dlC/BA)(dlB/A) |
| 155 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](gaCB/A)(pvC/B) |
| 156 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](gaCB/A)(dlC/B) |
| 157 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlCB/A)(pvC/B) |
| 158 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlCB/A)(dlC/B) |
| 159 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlC/BA)(gaB/A) |
| 160 | (iABCDE)(mABCDE)(dlED/CAB)[(dlE/D)](dlC/BA)(dlB/A) |

| | |
|---|---|
| 161 | (iABCDE)(mABCDE)(gaEDCB/A)(gaED/CB)[(dlE/D)](pvC/B) |
| 162 | (iABCDE)(mABCDE)(gaEDCB/A)(gaED/CB)[(dlE/D)](dlC/B) |
| 163 | (iABCDE)(mABCDE)(gaEDCB/A)(pvED/CB)[(dlE/D)](pvC/B) |
| 164 | (iABCDE)(mABCDE)(gaEDCB/A)(pvED/CB)[(dlE/D)](dlC/B) |
| 165 | (iABCDE)(mABCDE)(gaEDCB/A)(laED/CB)[(dlE/D)](pvC/B) |
| 166 | (iABCDE)(mABCDE)(gaEDCB/A)(laED/CB)[(dlE/D)](dlC/B) |
| 167 | (iABCDE)(mABCDE)(gaEDCB/A)(dlED/CB)[(dlE/D)](pvC/B) |
| 168 | (iABCDE)(mABCDE)(gaEDCB/A)(dlED/CB)[(dlE/D)](dlC/B) |
| 169 | (iABCDE)(mABCDE)(dlEDCB/A)(gaED/CB)[(dlE/D)](pvC/B) |
| 170 | (iABCDE)(mABCDE)(dlEDCB/A)(gaED/CB)[(dlE/D)](dlC/B) |
| 171 | (iABCDE)(mABCDE)(dlEDCB/A)(pvED/CB)[(dlE/D)](pvC/B) |
| 172 | (iABCDE)(mABCDE)(dlEDCB/A)(pvED/CB)[(dlE/D)](dlC/B) |
| 173 | (iABCDE)(mABCDE)(dlEDCB/A)(laED/CB)[(dlE/D)](pvC/B) |
| 174 | (iABCDE)(mABCDE)(dlEDCB/A)(laED/CB)[(dlE/D)](dlC/B) |
| 175 | (iABCDE)(mABCDE)(dlEDCB/A)(dlED/CB)[(dlE/D)](pvC/B) |
| 176 | (iABCDE)(mABCDE)(dlEDCB/A)(dlED/CB)[(dlE/D)](dlC/B) |
| 177 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(gaD/C)](gaB/A) |
| 178 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(pvD/C)](gaB/A) |
| 179 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(laD/C)](gaB/A) |
| 180 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(dlD/C)](gaB/A) |
| 181 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(gaD/C)](dlB/A) |
| 182 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(pvD/C)](dlB/A) |
| 183 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(laD/C)](dlB/A) |
| 184 | (iABCDE)(mABCDE)(dlE/DABC)(dlDC/BA)[(dlD/C)](dlB/A) |

# APPENDIX G

In this section, all the process alternatives generated for conceptual example related to separation of 4-component mixtures is given in the form of SFILES representation.

*Table G1: SFILES of generated process alternatives.*

| **Design no** | **SFILES** |
|---|---|
| 1 | (iABCD)(dlABC/D)(abA/BC)(dlB/C) |
| 2 | (iABCD)(dlABC/D)(dlA/BC)(dlB/C) |
| 3 | (iABCD)(dlABC/D)(lmA/BC)(dlB/C) |
| 4 | (iABCD)(gmABC/D)(abA/BC)(dlB/C) |
| 5 | (iABCD)(gmABC/D)(dlA/BC)(dlB/C) |
| 6 | (iABCD)(gmABC/D)(lmA/BC)(dlB/C) |
| 7 | (iABCD)(msABC/D)(abA/BC)(dlB/C) |
| 8 | (iABCD)(msABC/D)(dlA/BC)(dlB/C) |
| 9 | (iABCD)(msABC/D)(lmA/BC)(dlB/C) |
| 10 | (iABCD)(czA/BCD)(czBC/D)(dlB/C) |
| 11 | (iABCD)(czA/BCD)(dlBC/D)(dlB/C) |
| 12 | (iABCD)(czA/BCD)(msBC/D)(dlB/C) |
| 13 | (iABCD)(lmA/BCD)(czBC/D)(dlB/C) |
| 14 | (iABCD)(lmA/BCD)(dlBC/D)(dlB/C) |
| 15 | (iABCD)(lmA/BCD)(msBC/D)(dlB/C) |
| 16 | (iABCD)(dlA/BCD)(czBC/D)(dlB/C) |
| 17 | (iABCD)(dlA/BCD)(dlBC/D)(dlB/C) |
| 18 | (iABCD)(dlA/BCD)(msBC/D)(dlB/C) |
| 19 | (iABCD)(dlAB/CD)(lmA/B)[(dlC/D)] |
| 20 | (iABCD)(dlAB/CD)(gmA/B)[(dlC/D)] |
| 21 | (iABCD)(dlAB/CD)(msA/B)[(dlC/D)] |
| 22 | (iABCD)(msAB/CD)(lmA/B)[(dlC/D)] |
| 23 | (iABCD)(msAB/CD)(gmA/B)[(dlC/D)] |
| 24 | (iABCD)(msAB/CD)(msA/B)[(dlC/D)] |
| 25 | (iABCD)(abAB/CD)(lmA/B)[(dlC/D)] |
| 26 | (iABCD)(abAB/CD)(gmA/B)[(dlC/D)] |
| 27 | (iABCD)(abAB/CD)(msA/B)[(dlC/D)] |

# APPENDIX H

In this section, all the threshold values for the properties are given so that the separation techniques is feasible.

*Table H1: SFILES of generated process alternatives.*

| Separation Technique | Threshold values | Properties |
|---|---|---|
| Absorption[1] | 1.11 | Solubility parameter |
| Azeotropic distillation[1] | | Solubility parameter |
| Cryogenic distillation | 1.12,1.80 | Boiling point,Vapor pressure |
| Crystallization | 1.2 | Melting point |
| Desublimation | 30,1.1 | Triple point temperature, triple point temperature |
| Distillation | 1.01,1.05 | Boiling point,Vapor pressure |
| Extractive distillation[1] | 0,0 | Boiling point,Vapor pressure |
| Flash Operation | 1.23,10 | Boiling point,Vapor pressure |
| Gas separation membranes | 1.07,1.1 | Van der Waals volume, critical temp |
| Ion exchange | 1 | Ion charge |
| Leaching [1] | | Solubility parameter |
| Liquid-liquid extraction[1] | | Solubility parameter |
| Liquid membranes | 1.01,1.02,1.2 | Solubility parameter, radius of gyration, molar volume |
| Microfiltration | 2,1.9 | molecular diameter, molecular weight |
| Molecular sieve adsorption | 1.05,1.07,1.08,1.05 | Kinetic diameter, Van der Waals volume |
| Partial condensation | 1.9 | Boiling point |
| Pervaporation | 1.02.1 | Molar volume,solubility parameter |
| Stripping[1] | 0 | Solubility parameter |
| Sublimation | 30,1.1 | Triple point temperature, triple point temperature |
| Ultrafiltraion | 2,1.7 | molecular diameter, molecular weight |

[1]These techniques require a mass separating agent, which is, identified from solubility parameter and mixture properties such as selectivity, solubility.

# APPENDIX I

In this section, all the process alternatives generated for production of Cumene and Biodesiel are presented.

*Table I1: SFILES of generated process alternatives for production of Cumene.*

| Design no | SFILES |
|---|---|
| 1 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(gaED/C)(czE/D) |
| 2 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(gaED/C)(pvD/E) |
| 3 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(gaED/C)(laE/D) |
| 4 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(gaED/C)(dlE/D) |
| 5 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvC/DE)(czE/D) |
| 6 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvC/DE)(pvD/E) |
| 7 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvC/DE)(laE/D) |
| 8 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvC/DE)(dlE/D) |
| 9 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laED/C)(czE/D) |
| 10 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laED/C)(pvD/E) |
| 11 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laED/C)(laE/D) |
| 12 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laED/C)(dlE/D) |
| 13 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlED/C)(czE/D) |
| 14 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlED/C)(pvD/E) |
| 15 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlED/C)(laE/D) |
| 16 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlED/C)(dlE/D) |
| 17 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(czCE/D)(pvC/E) |
| 18 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(czCE/D)(laE/C) |
| 19 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(czCE/D)(dlE/C) |
| 20 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvCD/E)(gaD/C) |
| 21 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvCD/E)(czC/D) |
| 22 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvCD/E)(pvC/D) |
| 23 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvCD/E)(laD/C) |
| 24 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(pvCD/E)(dlD/C) |
| 25 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laE/DC)(gaD/C) |
| 26 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laE/DC)(czC/D) |
| 27 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laE/DC)(pvC/D) |
| 28 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laE/DC)(laD/C) |
| 29 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(laE/DC)(dlD/C) |
| 30 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlE/DC)(gaD/C) |
| 31 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlE/DC)(czC/D) |
| 32 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlE/DC)(pvC/D) |
| 33 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlE/DC)(laD/C) |
| 34 | (iC)[(iAB)](reABC/ABCDE)(gaEDC/AB)(dlE/DC)(dlD/C) |
| 35 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(gaED/C)(czE/D) |

| | |
|---|---|
| 36 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(gaED/C)(pvD/E) |
| 37 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(gaED/C)(laE/D) |
| 38 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(gaED/C)(dlE/D) |
| 39 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvC/DE)(czE/D) |
| 40 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvC/DE)(pvD/E) |
| 41 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvC/DE)(laE/D) |
| 42 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvC/DE)(dlE/D) |
| 43 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laED/C)(czE/D) |
| 44 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laED/C)(pvD/E) |
| 45 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laED/C)(laE/D) |
| 46 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laED/C)(dlE/D) |
| 47 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(czE/D) |
| 48 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(pvD/E) |
| 49 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(laE/D) |
| 50 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlED/C)(dlE/D) |
| 51 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(czCE/D)(pvC/E) |
| 52 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(czCE/D)(laE/C) |
| 53 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(czCE/D)(dlE/C) |
| 54 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvCD/E)(gaD/C) |
| 55 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvCD/E)(czC/D) |
| 56 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvCD/E)(pvC/D) |
| 57 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvCD/E)(laD/C) |
| 58 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(pvCD/E)(dlD/C) |
| 59 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laE/DC)(gaD/C) |
| 60 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laE/DC)(czC/D) |
| 61 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laE/DC)(pvC/D) |
| 62 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laE/DC)(laD/C) |
| 63 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(laE/DC)(dlD/C) |
| 64 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(gaD/C) |
| 65 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(czC/D) |
| 66 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(pvC/D) |
| 67 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(laD/C) |
| 68 | (iC)[(iAB)](reABC/ABCDE)(flEDC/AB)(dlE/DC)(dlD/C) |
| 69 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(gaED/C)(czE/D) |
| 70 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(gaED/C)(pvD/E) |
| 71 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(gaED/C)(laE/D) |
| 72 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(gaED/C)(dlE/D) |
| 73 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvC/DE)(czE/D) |
| 74 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvC/DE)(pvD/E) |
| 75 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvC/DE)(laE/D) |
| 76 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvC/DE)(dlE/D) |
| 77 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laED/C)(czE/D) |

| | |
|---|---|
| 78 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laED/C)(pvD/E) |
| 79 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laED/C)(laE/D) |
| 80 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laED/C)(dlE/D) |
| 81 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(czE/D) |
| 82 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(pvD/E) |
| 83 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(laE/D) |
| 84 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlED/C)(dlE/D) |
| 85 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(czCE/D)(pvC/E) |
| 86 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(czCE/D)(laE/C) |
| 87 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(czCE/D)(dlE/C) |
| 88 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvCD/E)(gaD/C) |
| 89 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvCD/E)(czC/D) |
| 90 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvCD/E)(pvC/D) |
| 91 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvCD/E)(laD/C) |
| 92 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(pvCD/E)(dlD/C) |
| 93 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laE/DC)(gaD/C) |
| 94 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laE/DC)(czC/D) |
| 95 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laE/DC)(pvC/D) |
| 96 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laE/DC)(laD/C) |
| 97 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(laE/DC)(dlD/C) |
| 98 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(gaD/C) |
| 99 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(czC/D) |
| 100 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(pvC/D) |
| 101 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(laD/C) |
| 102 | (iC)[(iAB)](reABC/ABCDE)(dlEDC/AB)(dlE/DC)(dlD/C) |
| 103 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(gaED/AB)(czE/D) |
| 104 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(gaED/AB)(pvD/E) |
| 105 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(gaED/AB)(laE/D) |
| 106 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(gaED/AB)(dlE/D) |
| 107 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(flED/AB)(czE/D) |
| 108 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(flED/AB)(pvD/E) |
| 109 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(flED/AB)(laE/D) |
| 110 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(flED/AB)(dlE/D) |
| 111 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlED/AB)(czE/D) |
| 112 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlED/AB)(pvD/E) |
| 113 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlED/AB)(laE/D) |
| 114 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlED/AB)(dlE/D) |
| 115 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(czE/DAB)(gaD/AB) |
| 116 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(czE/DAB)(flD/AB) |
| 117 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(czE/DAB)(dlD/AB) |
| 118 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(pvD/EAB)(flE/AB) |
| 119 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(pvD/EAB)(dlE/AB) |

| | |
|---|---|
| 120 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(gaD/AB) |
| 121 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(flD/AB) |
| 122 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(laE/DAB)(dlD/AB) |
| 123 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(gaD/AB) |
| 124 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(flD/AB) |
| 125 | (iC)[(iAB)](reABC/ABCDE)(pvC/DABE)(dlE/DAB)(dlD/AB) |
| 126 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(gaD/C) |
| 127 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(czC/D) |
| 128 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(pvC/D) |
| 129 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(laD/C) |
| 130 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaDC/AB)(dlD/C) |
| 131 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(gaD/C) |
| 132 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(czC/D) |
| 133 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(pvC/D) |
| 134 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(laD/C) |
| 135 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(flDC/AB)(dlD/C) |
| 136 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(gaD/C) |
| 137 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(czC/D) |
| 138 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(pvC/D) |
| 139 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(laD/C) |
| 140 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlDC/AB)(dlD/C) |
| 141 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaD/CAB)(gaC/AB) |
| 142 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaD/CAB)(flC/AB) |
| 143 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(gaD/CAB)(dlC/AB) |
| 144 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(czC/DAB)(gaD/AB) |
| 145 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(czC/DAB)(flD/AB) |
| 146 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(czC/DAB)(dlD/AB) |
| 147 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(pvC/DAB)(gaD/AB) |
| 148 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(pvC/DAB)(flD/AB) |
| 149 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(pvC/DAB)(dlD/AB) |
| 150 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(laD/CAB)(gaC/AB) |
| 151 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(laD/CAB)(flC/AB) |
| 152 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(laD/CAB)(dlC/AB) |
| 153 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlD/CAB)(gaC/AB) |
| 154 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlD/CAB)(flC/AB) |
| 155 | (iC)[(iAB)](reABC/ABCDE)(laE/DABC)(dlD/CAB)(dlC/AB) |
| 156 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(gaD/C) |
| 157 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(czC/D) |
| 158 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(pvC/D) |
| 159 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(laD/C) |
| 160 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaDC/AB)(dlD/C) |
| 161 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(gaD/C) |

| | |
|---|---|
| 162 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(czC/D) |
| 163 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(pvC/D) |
| 164 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(laD/C) |
| 165 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(flDC/AB)(dlD/C) |
| 166 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(gaD/C) |
| 167 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(czC/D) |
| 168 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(pvC/D) |
| 169 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(laD/C) |
| 170 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlDC/AB)(dlD/C) |
| 171 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaD/CAB)(gaC/AB) |
| 172 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaD/CAB)(flC/AB) |
| 173 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(gaD/CAB)(dlC/AB) |
| 174 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(gaD/AB) |
| 175 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(flD/AB) |
| 176 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(czC/DAB)(dlD/AB) |
| 177 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(pvC/DAB)(gaD/AB) |
| 178 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(pvC/DAB)(flD/AB) |
| 179 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(pvC/DAB)(dlD/AB) |
| 180 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(laD/CAB)(gaC/AB) |
| 181 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(laD/CAB)(flC/AB) |
| 182 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(laD/CAB)(dlC/AB) |
| 183 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(gaC/AB) |
| 184 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(flC/AB) |
| 185 | (iC)[(iAB)](reABC/ABCDE)(dlE/DABC)(dlD/CAB)(dlC/AB) |
| 186 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(czE/D)](gaC/AB) |
| 187 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(pvD/E)](gaC/AB) |
| 188 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(laE/D)](gaC/AB) |
| 189 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(dlE/D)](gaC/AB) |
| 190 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(czE/D)](flC/AB) |
| 191 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(pvD/E)](flC/AB) |
| 192 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(laE/D)](flC/AB) |
| 193 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(dlE/D)](flC/AB) |
| 194 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(czE/D)](dlC/AB) |
| 195 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(pvD/E)](dlC/AB) |
| 196 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(laE/D)](dlC/AB) |
| 197 | (iC)[(iAB)](reABC/ABCDE)(gaED/CAB)[(dlE/D)](dlC/AB) |
| 198 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(czE/D)](gaC/AB) |
| 199 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(pvD/E)](gaC/AB) |
| 200 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(laE/D)](gaC/AB) |
| 201 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(dlE/D)](gaC/AB) |
| 202 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(czE/D)](flC/AB) |
| 203 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(pvD/E)](flC/AB) |

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|---|---|
| 204 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(laE/D)](flC/AB) |
| 205 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(dlE/D)](flC/AB) |
| 206 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(czE/D)](dlC/AB) |
| 207 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(pvD/E)](dlC/AB) |
| 208 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(laE/D)](dlC/AB) |
| 209 | (iC)[(iAB)](reABC/ABCDE)(laED/CAB)[(dlE/D)](dlC/AB) |
| 210 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(czE/D)](gaC/AB) |
| 211 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(pvD/E)](gaC/AB) |
| 212 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(laE/D)](gaC/AB) |
| 213 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(dlE/D)](gaC/AB) |
| 214 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(czE/D)](flC/AB) |
| 215 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(pvD/E)](flC/AB) |
| 216 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(laE/D)](flC/AB) |
| 217 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(dlE/D)](flC/AB) |
| 218 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(czE/D)](dlC/AB) |
| 219 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(pvD/E)](dlC/AB) |
| 220 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(laE/D)](dlC/AB) |
| 221 | (iC)[(iAB)](reABC/ABCDE)(dlED/CAB)[(dlE/D)](dlC/AB) |
| 222 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(pvC/E)](gaD/AB) |
| 223 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(laE/C)](gaD/AB) |
| 224 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(dlE/C)](gaD/AB) |
| 225 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(pvC/E)](flD/AB) |
| 226 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(laE/C)](flD/AB) |
| 227 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(dlE/C)](flD/AB) |
| 228 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(pvC/E)](dlD/AB) |
| 229 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(laE/C)](dlD/AB) |
| 230 | (iC)[(iAB)](reABC/ABCDE)(czCE/DAB)[(dlE/C)](dlD/AB) |
| 231 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(gaD/C)](flE/AB) |
| 232 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(czC/D)](flE/AB) |
| 233 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(pvC/D)](flE/AB) |
| 234 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(laD/C)](flE/AB) |
| 235 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(dlD/C)](flE/AB) |
| 236 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(gaD/C)](dlE/AB) |
| 237 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(czC/D)](dlE/AB) |
| 238 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(pvC/D)](dlE/AB) |
| 239 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(laD/C)](dlE/AB) |
| 240 | (iC)[(iAB)](reABC/ABCDE)(pvCD/EAB)[(dlD/C)](dlE/AB) |

*Table I1: SFILES of generated process alternatives for production of Cumene.*

| Design no | SFILES |
|---|---|
| 1 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvDA/C)(gaA/D) |
| 2 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvDA/C)(lmA/D) |
| 3 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvDA/C)(pvD/A) |
| 4 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvDA/C)(laA/D) |
| 5 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvDA/C)(dlD/A) |
| 6 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(gaCA/D)(pvA/C) |
| 7 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(gaCA/D)(flC/A) |
| 8 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(gaCA/D)(dlC/A) |
| 9 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(lmCA/D)(pvA/C) |
| 10 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(lmCA/D)(flC/A) |
| 11 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(lmCA/D)(dlC/A) |
| 12 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvD/AC)(pvA/C) |
| 13 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvD/AC)(flC/A) |
| 14 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(pvD/AC)(dlC/A) |
| 15 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(laCA/D)(pvA/C) |
| 16 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(laCA/D)(flC/A) |
| 17 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(laCA/D)(dlC/A) |
| 18 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlCD/A)(lmC/D) |
| 19 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlCD/A)(pvD/C) |
| 20 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlCD/A)(laC/D) |
| 21 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlCD/A)(flC/D) |
| 22 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlCD/A)(dlC/D) |
| 23 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(flC/DA)(gaA/D) |
| 24 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(flC/DA)(lmA/D) |
| 25 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(flC/DA)(pvD/A) |
| 26 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(flC/DA)(laA/D) |
| 27 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(flC/DA)(dlD/A) |
| 28 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlC/DA)(gaA/D) |
| 29 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlC/DA)(lmA/D) |
| 30 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlC/DA)(pvD/A) |
| 31 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlC/DA)(laA/D) |
| 32 | (iB)[(iA)](reAB/ABCD)(dlDCA/B)(dlC/DA)(dlD/A) |
| 33 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(gaB/D) |
| 34 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(czD/B) |
| 35 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(lmB/D) |
| 36 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(pvD/B) |
| 37 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(laB/D) |
| 38 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaA/BD)(dlD/B) |
| 39 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(gaB/D) |
| 40 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(czD/B) |

| | |
|---|---|
| 41 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(lmB/D) |
| 42 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(pvD/B) |
| 43 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(laB/D) |
| 44 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmA/BD)(dlD/B) |
| 45 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(gaB/D) |
| 46 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(czD/B) |
| 47 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(lmB/D) |
| 48 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(pvD/B) |
| 49 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(laB/D) |
| 50 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvDB/A)(dlD/B) |
| 51 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(gaB/D) |
| 52 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(czD/B) |
| 53 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(lmB/D) |
| 54 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(pvD/B) |
| 55 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(laB/D) |
| 56 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laA/BD)(dlD/B) |
| 57 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlDA/B)(gaA/D) |
| 58 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlDA/B)(lmA/D) |
| 59 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlDA/B)(pvD/A) |
| 60 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlDA/B)(laA/D) |
| 61 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlDA/B)(dlD/A) |
| 62 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(gaA/B) |
| 63 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(czA/B) |
| 64 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(lmA/B) |
| 65 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(pvB/A) |
| 66 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(laA/B) |
| 67 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(dlD/AB)(dlA/B) |
| 68 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(gaA/B) |
| 69 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(czA/B) |
| 70 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(lmA/B) |
| 71 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(pvB/A) |
| 72 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(laA/B) |
| 73 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(gaAB/D)(dlA/B) |
| 74 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(czAD/B)(gaA/D) |
| 75 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(czAD/B)(lmA/D) |
| 76 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(czAD/B)(pvD/A) |
| 77 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(czAD/B)(laA/D) |
| 78 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(czAD/B)(dlD/A) |
| 79 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(gaA/B) |
| 80 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(czA/B) |
| 81 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(lmA/B) |
| 82 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(pvB/A) |

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| 83 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(laA/B) |
| 84 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(lmAB/D)(dlA/B) |
| 85 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(gaA/B) |
| 86 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(czA/B) |
| 87 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(lmA/B) |
| 88 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(pvB/A) |
| 89 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(laA/B) |
| 90 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(pvD/BA)(dlA/B) |
| 91 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(gaA/B) |
| 92 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(czA/B) |
| 93 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(lmA/B) |
| 94 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(pvB/A) |
| 95 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(laA/B) |
| 96 | (iB)[(iA)](reAB/ABCD)(pvDBA/C)(laAB/D)(dlA/B) |
| 97 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(gaCA/B)(pvA/C) |
| 98 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(gaCA/B)(flC/A) |
| 99 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(gaCA/B)(dlC/A) |
| 100 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(lmCA/B)(pvA/C) |
| 101 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(lmCA/B)(flC/A) |
| 102 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(lmCA/B)(dlC/A) |
| 103 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvB/AC)(pvA/C) |
| 104 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvB/AC)(flC/A) |
| 105 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvB/AC)(dlC/A) |
| 106 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(laCA/B)(pvA/C) |
| 107 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(laCA/B)(flC/A) |
| 108 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(laCA/B)(dlC/A) |
| 109 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlCA/B)(pvA/C) |
| 110 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlCA/B)(flC/A) |
| 111 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlCA/B)(dlC/A) |
| 112 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(gaA/B) |
| 113 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(czA/B) |
| 114 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(lmA/B) |
| 115 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(pvB/A) |
| 116 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(laA/B) |
| 117 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(pvBA/C)(dlA/B) |
| 118 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(gaA/B) |
| 119 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(czA/B) |
| 120 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(lmA/B) |
| 121 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(pvB/A) |
| 122 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(laA/B) |
| 123 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(flC/AB)(dlA/B) |
| 124 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(gaA/B) |

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| 125 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(czA/B) |
| 126 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(lmA/B) |
| 127 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(pvB/A) |
| 128 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(laA/B) |
| 129 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(dlC/AB)(dlA/B) |
| 130 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(czAC/B)(pvA/C) |
| 131 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(czAC/B)(flC/A) |
| 132 | (iB)[(iA)](reAB/ABCD)(gaCAB/D)(czAC/B)(dlC/A) |
| 133 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvDA/C)(gaA/D) |
| 134 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvDA/C)(lmA/D) |
| 135 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvDA/C)(pvD/A) |
| 136 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvDA/C)(laA/D) |
| 137 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvDA/C)(dlD/A) |
| 138 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(gaCA/D)(pvA/C) |
| 139 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(gaCA/D)(flC/A) |
| 140 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(gaCA/D)(dlC/A) |
| 141 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(lmCA/D)(pvA/C) |
| 142 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(lmCA/D)(flC/A) |
| 143 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(lmCA/D)(dlC/A) |
| 144 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvD/AC)(pvA/C) |
| 145 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvD/AC)(flC/A) |
| 146 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(pvD/AC)(dlC/A) |
| 147 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(laCA/D)(pvA/C) |
| 148 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(laCA/D)(flC/A) |
| 149 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(laCA/D)(dlC/A) |
| 150 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlCD/A)(lmC/D) |
| 151 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlCD/A)(pvD/C) |
| 152 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlCD/A)(laC/D) |
| 153 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlCD/A)(flC/D) |
| 154 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlCD/A)(dlC/D) |
| 155 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(flC/DA)(gaA/D) |
| 156 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(flC/DA)(lmA/D) |
| 157 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(flC/DA)(pvD/A) |
| 158 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(flC/DA)(laA/D) |
| 159 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(flC/DA)(dlD/A) |
| 160 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlC/DA)(gaA/D) |
| 161 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlC/DA)(lmA/D) |
| 162 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlC/DA)(pvD/A) |
| 163 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlC/DA)(laA/D) |
| 164 | (iB)[(iA)](reAB/ABCD)(czCAD/B)(dlC/DA)(dlD/A) |
| 165 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(gaCA/B)(pvA/C) |
| 166 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(gaCA/B)(flC/A) |

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| 167 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(gaCA/B)(dlC/A) |
| 168 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(lmCA/B)(pvA/C) |
| 169 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(lmCA/B)(flC/A) |
| 170 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(lmCA/B)(dlC/A) |
| 171 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvB/AC)(pvA/C) |
| 172 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvB/AC)(flC/A) |
| 173 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvB/AC)(dlC/A) |
| 174 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(laCA/B)(pvA/C) |
| 175 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(laCA/B)(flC/A) |
| 176 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(laCA/B)(dlC/A) |
| 177 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlCA/B)(pvA/C) |
| 178 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlCA/B)(flC/A) |
| 179 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlCA/B)(dlC/A) |
| 180 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvBA/C)(gaA/B) |
| 181 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvBA/C)(czA/B) |
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| 183 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvBA/C)(pvB/A) |
| 184 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvBA/C)(laA/B) |
| 185 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(pvBA/C)(dlA/B) |
| 186 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(gaA/B) |
| 187 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(czA/B) |
| 188 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(lmA/B) |
| 189 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(pvB/A) |
| 190 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(laA/B) |
| 191 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(flC/AB)(dlA/B) |
| 192 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(gaA/B) |
| 193 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(czA/B) |
| 194 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(lmA/B) |
| 195 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(pvB/A) |
| 196 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(laA/B) |
| 197 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(dlC/AB)(dlA/B) |
| 198 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(czAC/B)(pvA/C) |
| 199 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(czAC/B)(flC/A) |
| 200 | (iB)[(iA)](reAB/ABCD)(lmCAB/D)(czAC/B)(dlC/A) |
| 201 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(gaCA/B)(pvA/C) |
| 202 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(gaCA/B)(flC/A) |
| 203 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(gaCA/B)(dlC/A) |
| 204 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(lmCA/B)(pvA/C) |
| 205 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(lmCA/B)(flC/A) |
| 206 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(lmCA/B)(dlC/A) |
| 207 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvB/AC)(pvA/C) |
| 208 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvB/AC)(flC/A) |

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| 209 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvB/AC)(dlC/A) |
| 210 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(laCA/B)(pvA/C) |
| 211 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(laCA/B)(flC/A) |
| 212 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(laCA/B)(dlC/A) |
| 213 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlCA/B)(pvA/C) |
| 214 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlCA/B)(flC/A) |
| 215 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlCA/B)(dlC/A) |
| 216 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(gaA/B) |
| 217 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(czA/B) |
| 218 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(lmA/B) |
| 219 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(pvB/A) |
| 220 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(laA/B) |
| 221 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(pvBA/C)(dlA/B) |
| 222 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(gaA/B) |
| 223 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(czA/B) |
| 224 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(lmA/B) |
| 225 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(pvB/A) |
| 226 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(laA/B) |
| 227 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(flC/AB)(dlA/B) |
| 228 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlC/AB)(gaA/B) |
| 229 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlC/AB)(czA/B) |
| 230 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlC/AB)(lmA/B) |
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| 232 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlC/AB)(laA/B) |
| 233 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(dlC/AB)(dlA/B) |
| 234 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(czAC/B)(pvA/C) |
| 235 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(czAC/B)(flC/A) |
| 236 | (iB)[(iA)](reAB/ABCD)(pvD/BAC)(czAC/B)(dlC/A) |
| 237 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(gaCA/B)(pvA/C) |
| 238 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(gaCA/B)(flC/A) |
| 239 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(gaCA/B)(dlC/A) |
| 240 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(lmCA/B)(pvA/C) |
| 241 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(lmCA/B)(flC/A) |
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| 243 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvB/AC)(pvA/C) |
| 244 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvB/AC)(flC/A) |
| 245 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvB/AC)(dlC/A) |
| 246 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(laCA/B)(pvA/C) |
| 247 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(laCA/B)(flC/A) |
| 248 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(laCA/B)(dlC/A) |
| 249 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlCA/B)(pvA/C) |
| 250 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlCA/B)(flC/A) |

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| 251 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlCA/B)(dlC/A) |
| 252 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(gaA/B) |
| 253 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(czA/B) |
| 254 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(lmA/B) |
| 255 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(pvB/A) |
| 256 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(laA/B) |
| 257 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(pvBA/C)(dlA/B) |
| 258 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(gaA/B) |
| 259 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(czA/B) |
| 260 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(lmA/B) |
| 261 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(pvB/A) |
| 262 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(laA/B) |
| 263 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(flC/AB)(dlA/B) |
| 264 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(gaA/B) |
| 265 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(czA/B) |
| 266 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(lmA/B) |
| 267 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(pvB/A) |
| 268 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(laA/B) |
| 269 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(dlC/AB)(dlA/B) |
| 270 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(czAC/B)(pvA/C) |
| 271 | (iB)[(iA)](reAB/ABCD)(laCAB/D)(czAC/B)(flC/A) |
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| 275 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaA/BD)(lmB/D) |
| 276 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaA/BD)(pvD/B) |
| 277 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaA/BD)(laB/D) |
| 278 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaA/BD)(dlD/B) |
| 279 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(gaB/D) |
| 280 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(czD/B) |
| 281 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(lmB/D) |
| 282 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(pvD/B) |
| 283 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(laB/D) |
| 284 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmA/BD)(dlD/B) |
| 285 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(gaB/D) |
| 286 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(czD/B) |
| 287 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(lmB/D) |
| 288 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(pvD/B) |
| 289 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(laB/D) |
| 290 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvDB/A)(dlD/B) |
| 291 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(gaB/D) |
| 292 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(czD/B) |

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| 293 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(lmB/D) |
| 294 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(pvD/B) |
| 295 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(laB/D) |
| 296 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laA/BD)(dlD/B) |
| 297 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlDA/B)(gaA/D) |
| 298 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlDA/B)(lmA/D) |
| 299 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlDA/B)(pvD/A) |
| 300 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlDA/B)(laA/D) |
| 301 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlDA/B)(dlD/A) |
| 302 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(gaA/B) |
| 303 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(czA/B) |
| 304 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(lmA/B) |
| 305 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(pvB/A) |
| 306 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(laA/B) |
| 307 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(dlD/AB)(dlA/B) |
| 308 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(gaA/B) |
| 309 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(czA/B) |
| 310 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(lmA/B) |
| 311 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(pvB/A) |
| 312 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(laA/B) |
| 313 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(gaAB/D)(dlA/B) |
| 314 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(czAD/B)(gaA/D) |
| 315 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(czAD/B)(lmA/D) |
| 316 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(czAD/B)(pvD/A) |
| 317 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(czAD/B)(laA/D) |
| 318 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(czAD/B)(dlD/A) |
| 319 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(gaA/B) |
| 320 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(czA/B) |
| 321 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(lmA/B) |
| 322 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(pvB/A) |
| 323 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(laA/B) |
| 324 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(lmAB/D)(dlA/B) |
| 325 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(gaA/B) |
| 326 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(czA/B) |
| 327 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(lmA/B) |
| 328 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(pvB/A) |
| 329 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(laA/B) |
| 330 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(pvD/BA)(dlA/B) |
| 331 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(gaA/B) |
| 332 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(czA/B) |
| 333 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(lmA/B) |
| 334 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(pvB/A) |

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| 335 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(laA/B) |
| 336 | (iB)[(iA)](reAB/ABCD)(flC/DAB)(laAB/D)(dlA/B) |
| 337 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(gaB/D) |
| 338 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(czD/B) |
| 339 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(lmB/D) |
| 340 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(pvD/B) |
| 341 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(laB/D) |
| 342 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaA/BD)(dlD/B) |
| 343 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(gaB/D) |
| 344 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(czD/B) |
| 345 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(lmB/D) |
| 346 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(pvD/B) |
| 347 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(laB/D) |
| 348 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmA/BD)(dlD/B) |
| 349 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(gaB/D) |
| 350 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(czD/B) |
| 351 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(lmB/D) |
| 352 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(pvD/B) |
| 353 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(laB/D) |
| 354 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvDB/A)(dlD/B) |
| 355 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(gaB/D) |
| 356 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(czD/B) |
| 357 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(lmB/D) |
| 358 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(pvD/B) |
| 359 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(laB/D) |
| 360 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laA/BD)(dlD/B) |
| 361 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlDA/B)(gaA/D) |
| 362 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlDA/B)(lmA/D) |
| 363 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlDA/B)(pvD/A) |
| 364 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlDA/B)(laA/D) |
| 365 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlDA/B)(dlD/A) |
| 366 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(gaA/B) |
| 367 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(czA/B) |
| 368 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(lmA/B) |
| 369 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(pvB/A) |
| 370 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(laA/B) |
| 371 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(dlD/AB)(dlA/B) |
| 372 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(gaA/B) |
| 373 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(czA/B) |
| 374 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(lmA/B) |
| 375 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(pvB/A) |
| 376 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(laA/B) |

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| 377 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(gaAB/D)(dlA/B) |
| 378 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(czAD/B)(gaA/D) |
| 379 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(czAD/B)(lmA/D) |
| 380 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(czAD/B)(pvD/A) |
| 381 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(czAD/B)(laA/D) |
| 382 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(czAD/B)(dlD/A) |
| 383 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(gaA/B) |
| 384 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(czA/B) |
| 385 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(lmA/B) |
| 386 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(pvB/A) |
| 387 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(laA/B) |
| 388 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(lmAB/D)(dlA/B) |
| 389 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(gaA/B) |
| 390 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(czA/B) |
| 391 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(lmA/B) |
| 392 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(pvB/A) |
| 393 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(laA/B) |
| 394 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(pvD/BA)(dlA/B) |
| 395 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(gaA/B) |
| 396 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(czA/B) |
| 397 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(lmA/B) |
| 398 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(pvB/A) |
| 399 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(laA/B) |
| 400 | (iB)[(iA)](reAB/ABCD)(dlC/DAB)(laAB/D)(dlA/B) |
| 401 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(pvA/C)](gaB/D) |
| 402 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](gaB/D) |
| 403 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](gaB/D) |
| 404 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(pvA/C)](czD/B) |
| 405 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](czD/B) |
| 406 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](czD/B) |
| 407 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(pvA/C)](lmB/D) |
| 408 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](lmB/D) |
| 409 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](lmB/D) |
| 410 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(pvA/C)](pvD/B) |
| 411 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](pvD/B) |
| 412 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](pvD/B) |
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| 414 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](laB/D) |
| 415 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](laB/D) |
| 416 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(pvA/C)](dlD/B) |
| 417 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(flC/A)](dlD/B) |
| 418 | (iB)[(iA)](reAB/ABCD)(gaCA/BD)[(dlC/A)](dlD/B) |

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| 419 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](gaB/D) |
| 420 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](gaB/D) |
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| 422 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](czD/B) |
| 423 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](czD/B) |
| 424 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(dlC/A)](czD/B) |
| 425 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](lmB/D) |
| 426 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](lmB/D) |
| 427 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(dlC/A)](lmB/D) |
| 428 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](pvD/B) |
| 429 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](pvD/B) |
| 430 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(dlC/A)](pvD/B) |
| 431 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](laB/D) |
| 432 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](laB/D) |
| 433 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(dlC/A)](laB/D) |
| 434 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(pvA/C)](dlD/B) |
| 435 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(flC/A)](dlD/B) |
| 436 | (iB)[(iA)](reAB/ABCD)(lmCA/BD)[(dlC/A)](dlD/B) |
| 437 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(gaB/D)](pvA/C) |
| 438 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(czD/B)](pvA/C) |
| 439 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(lmB/D)](pvA/C) |
| 440 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(pvD/B)](pvA/C) |
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| 442 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(dlD/B)](pvA/C) |
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| 447 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(laB/D)](flC/A) |
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| 450 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(czD/B)](dlC/A) |
| 451 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(lmB/D)](dlC/A) |
| 452 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(pvD/B)](dlC/A) |
| 453 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(laB/D)](dlC/A) |
| 454 | (iB)[(iA)](reAB/ABCD)(pvDB/AC)[(dlD/B)](dlC/A) |
| 455 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(pvA/C)](gaB/D) |
| 456 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(flC/A)](gaB/D) |
| 457 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(dlC/A)](gaB/D) |
| 458 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(pvA/C)](czD/B) |
| 459 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(flC/A)](czD/B) |
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| 461 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(pvA/C)](lmB/D) |
| 462 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(flC/A)](lmB/D) |
| 463 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(dlC/A)](lmB/D) |
| 464 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(pvA/C)](pvD/B) |
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| 470 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(pvA/C)](dlD/B) |
| 471 | (iB)[(iA)](reAB/ABCD)(laCA/BD)[(flC/A)](dlD/B) |
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| 493 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(lmC/D)](laA/B) |
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| 495 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(laC/D)](laA/B) |
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| 497 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(dlC/D)](laA/B) |
| 498 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(lmC/D)](dlA/B) |
| 499 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(pvD/C)](dlA/B) |
| 500 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(laC/D)](dlA/B) |
| 501 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(flC/D)](dlA/B) |
| 502 | (iB)[(iA)](reAB/ABCD)(dlCD/AB)[(dlC/D)](dlA/B) |

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