SELECTION AND UTILIZATION OF CRITERIA FOR PROCESS DEVELOPMENT IN GREEN PRODUCTION OF ORGANIC CHEMICALS

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ABSTRACT

SELECTION AND UTILIZATION OF CRITERIA FOR PROCESS DEVELOPMENT IN GREEN PRODUCTION OF ORGANIC CHEMICALS

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Sustainability and green engineering are two main concepts considered throughout this study. Sustainability deals with the utilization of renewable and replaceable sugar-based twelve most promising building blocks included in the report prepared by U.S. Department of Energy and green engineering concept is related with the incorporation of environmental performance criteria to chemical process design. Process performance criteria at the conceptual design stage are selected as persistence, bioaccumulation and aquatic toxicity, economical potential of the processes, atom & mass efficiency of the processes and the relationship between Gibbs free energy of reaction values and economical potential. It is observed that bioaccumulation potentials of both the raw materials and products are low. Petrochemical raw materials are more persistent in air than the bio-based ones. The aquatic toxicity of bio-based raw materials is low; whereas some of the petrochemicals are moderately toxic and allyl alcohol and acrylonitrile among the petrochemicals are classified as highly toxic. Bio -based routes are not economically feasible with 2002 market prices. Atom and mass efficiencies of petrochemical reactions for a group of chemicals are higher than bio-based ones due to mostly addition or substitution reactions. Among high number of products, 1,3 propanediol production from glycerol with two microorganisms is analyzed at

preliminary design stage. Process performance criteria are selected as material and energy consumption, cooling water requirement, CO, CO_2, SO_2 and NO_X emissions to the atmosphere per unit of 1,3 propanediol production. *Klebsiella pneumoniae* process requires less cooling water, but it is less energy efficient and causes higher emissions.

Keywords: Sustainability, Green Engineering, Process performance criteria,
1,3 propanediol

ÖZ

ORGANİK KİMYASALLARIN ÇEVREYE DUYARLI ÜRETİMİNDE PROSES GELİŞTİRME KRİTERLERİNİN SEÇİMİ VE UYGULANMASI

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Bu çalışmada, üzerinde durulan iki önemli kavram sürdürülebilirlik ve çevreye duyarlı mühendisliktir. Sürdürülebilirlik, Amerikan Enerji Bakanlığı tarafından hazırlanmış raporda sözü edilen yenilenebilir ve değiştirilebilir on iki ümit veren şeker temelli yapıtaşının hammadde olarak uygulanmasıyla, çevreye duyarlı mühendislik ise çevresel performans kriterlerinin kimyasal tasarım sürecine dahil edilmesiyle ilişkilidir. Kavramsal tasarım aşaması için, bozunmaya karşı direnç, biyolojik birikim ve sudaki toksik etki, süreçlerin ekonomik potansiyelleri, atom ve kütle verimliliği, tepkimelerin Gibbs serbest enerji değerleri ile ekonomik potansiyel arasındaki ilişki, süreç performans kriterleri olarak seçilmiştir. Biyolojik birikiminin incelenen hammaddeler ve ürünler için düşük olduğu gözlenmiştir. Petrokimyasal hammaddelerin havada bozunmaya karşı direnci biyolojik hammaddelerden daha yüksektir. Biyolojik hammaddelerin sudaki toksik etkisi düşükken, petrokimyasalların bir kısmı orta seviyede toksik, allyl alkol ve akrilonitril ise oldukça toksiktir. Biyolojik üretim yolları 2002 pazar fiyatları dikkate alındığında ekonomik değildir. Bazı kimyasallar için atom ve kütle verimliliği petrokimyasal yollar için çoğunlukla ekleme ve yer değiştirme tepkimeleri nedeniyle biyolojik yollara oranla daha yüksektir. Çok sayıda ürün

arasından seçilen 1,3 propandiolün gliserolü hammadde olarak kullanabilen iki farklı mikroorganizma tarafından üretimi ön tasarım aşamasında incelenmiştir. Süreç performans kriterleri, üretilen 1,3 propandiol başına madde ve enerji tüketimi, soğutma suyu ihtiyacı, karbonmonoksit, karbondioksit, kükürtdioksit ve azot oksitlerinin havaya salınımını içermektedir. *Klebsiella pneumoniae* ile üretimde daha az soğutma suyu gereksinimi olmasına rağmen, enerji açısından daha az verimli olduğu ve daha yüksek gaz salınımı olduğu bulunmuştur.

Anahtar Kelimeler: Sürdürülebilirlik, çevreye duyarlı mühendislik, çevresel performans kriterleri, 1,3 propandiol

To My Family

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LIST OF SYMBOLS AND ABBREVIATIONS

AA	Acetic Acid
AOPWIN	Atmospheric Oxidation Program
AP	Acidification Potential
BA	Butyric Acid
BCF	Bioconcentration Factor
BCFWIN	Bioconcentration Factor Program
BDHL	Biodegradation Half-life
BDO	Butanediol
BE	Efficiency of the Boiler
BIOWIN	Biodegradation Probability Program
BOD	Biological Oxygen Demand
BPEO	Best Practicable Environmental Option
CTAM	Critical Air Mass
CTWM	Critical Water Mass
C.butyricum	*Clostridium butyricum*
ChV	Chronic Value
cm	Centimeter
cm^3	Cubic centimeter
CO_2	Carbon dioxide
c_{pi}^{0}	Heat Capacity of the i th Chemical
CW	Cooling Water
D	Dilution Rate
DBE	Dibutyl ether
EC	Effect Concentration
ECOSAR	Ecosystem Risk Program
ED	Energy Demand of the unit per year

EF	Emission Factor
EI	Environmental Index
ELF	Environmental Load Factor
EP	Eutrofication Potential
EPA	Environmental Protection Agency
EPISuite	Estimation Programs Interface Suited for Windows
ER	Ecological Risk
FDCA	2, 5 Furan Dicarboxylic Acid
FV	Fuel Value
GABA	Gamma-Butyric Acid
GBL	Gamma Butyrolactone
GWI	Global Warming Impact
GWP	Global Warming Potential
h	Hours
$\hat{H}_{steam}$	Enthalpy of steam
H_2	Hydrogen
H_2O	Water
HBL	Hydroxybutyrolactone
HCl	Hydrochloric Acid
3-HPA	3- Hydroxypropionic Acid
HTP	Human Toxicity Potential
j	Joule
K	Kelvin
KCN	Potassium Cyanide
km^2	Kilometer Square
K.pneumoniae	*Klebsiella pneumoniae*
KOWWIN	Octanol-Water Partition Coefficient Program
kPa	Kilopascal
kW.h	Kilowatt hour
(l)	Liquid

l	Liter
lb	Pound mass
LC	Lethal Concentration
LOAEL	Lowest Observable Adverse Effect Level
$\log K_{OW}$	Logaritmic Value of Octanol-Water Partition Coefficient
$\dot{m}_{steam}$	Mass flow rate of steam
$\dot{m}_{water}$	Mass flow rate of water
ME	The Efficiency of the Electric Motor
m	Meter
mg	Milligrams
MTBE	Methyl Tertiary Butyl Ether
Na	Sodium
N_2	Nitrogen
NE	Not estimated
NMP	N-Methyl Pyrrolidone
NO_x	Nitrous oxides
NOAEL	No Observable Adverse Effect Level
O_2	Oxygen
ODP	Ozone Depletion Potential
P	Pressure
P2	Pollution Prevention
PBT	Persistence Bioaccumulation Toxicity
PCR	Potential Chemical Risk
PDO	Propanediol
PEI	Potential Environmental Impact
PEL	Permissible Exposure Levels
ppm	Parts per million
Q_{req}	Heat Requirement
RD	Resource Depletion

REL	Recommended Exposure Level
RfC	Reference Concentration
RfD	Reference Dose
sec	Second
SF	Cancer Potency Slope Factor
SFP	Smog Formation Potential
SG	Syngas
SMD	Solid Mass Disposal
SMILES	Simplified Molecular Input Line Entry System
SO_2	Sulfur dioxide
SPI	Sustainable Process Index
SRC	Syracuse Research Corporation
SR	Safety Risk
SW	Salt-water
T	Temperature
THF	Tetrahydrofuran
TLV	Threshold Limit Value
wt %	Weight percent
$\dot{W}_s$	Shaft-Work
$Y_{Ac/S}$	Steady-state yield coefficient for acetic acid
$Y_{But/S}$	Steady-state yield coefficient for butyric acid
$Y_{PD/S}$	Steady-state yield coefficient for 1,3 propanediol
$Y_{X/S}$	Steady-state yield coefficient for biomass
Δ	Economical Potential
Δ’	Economical Potential plus Manufacturing Cost
$\Delta a_j, \Delta b_j, \Delta c_j, \Delta d_j$	Heat Capacity Coefficients
$\Delta \dot{E}_K$	Kinetic energy change
$\Delta \dot{E}_p$	Potential energy change

ΔG	Free energy changes of chemicals
ΔG_{rxn}^{0}	Free energy of reactions at standard state
ΔH_{f}^{0}	Enthalpy of formation
ΔH^{0}_{vap}	Enthalpy of vaporization
υ_i	Stoichiometric coefficient of the chemicals

CHAPTER 1

INTRODUCTION

Chemical and allied industries contribute to the progress of human life providing manufacturing of products and goods in various industries, such as: pharmaceutical, petrochemical, food and textile industries [1]. Unfortunately, developments have been mainly focused on economic prosperity and efforts to bring better living conditions have resulted in the depletion of natural resources and inevitable global environmental problems [2 & 3]. Although natural resources belong to all humanity, the fast economic growth and the present wasteful lifestyle in developed countries have caused large resource consumption resulting in environmental degradation and social inequity for poorer societies [4].

This perception resulted in the formulation of a new concept of development that incorporates economical, environmental and societal concerns for technological progress. This approach is called sustainable development which is defined in the Brutland Report in 1987 as 'Sustainable development is the development which meets the needs of the present without compromising the ability of future generations to meet their own needs' [5]. Clearly, the goal of sustainable development is not only technological but also societal. The creation of economically feasible and environmentally-friendly processes requires the efforts of chemical engineers in the development of sustainable processes [4]. Chemical engineering discipline includes design and operation of process plants, consideration of process integration, economical analysis of the processes and safety. In the last two decades, chemical engineers have started to consider the integration of environmental issues into process plant design and operation.

First, in the narrowest sense, "end-of-pipe approach" focusing on the control of pollutant releases, treatment of waste streams, reducing the toxic chemicals and pollutant amounts

in the transfer lines and discharges are included in the process design. However, the end–of-pipe approach focused on the problems created by the operations rather than on the causes of environmental problems [3 & 6].

A more popular approach is waste minimization, which incorporates source reduction and recycling to decrease the amount and risks of hazardous wastes [7].

A more effective and proactive approach, pollution prevention (P2) has gained importance, which is different from waste minimization and classical pollution control. Pollution prevention adopts the policy of preventing or reducing pollution during its generation. Accordingly, when pollution cannot be prevented, hazardous substances should be recycled or treated in an environmentally acceptable manner. Disposal or release of hazardous substances to the environment should be the last choice and the releases should be environmentally sound [7]. The evaluation of the P2 concerns of the chemicals requires the life cycle analysis, which includes quantifying the full range of environmental impacts of a product in all processing steps starting from pretreatment of raw material to the final treatment of the desired product and disposal of wastes [8].

The incorporation of P2 considerations into process design brings a new concept called 'green engineering'. Green engineering focuses on causing as little environmental impact as possible during the design and operation of chemical processes. Green engineering aims higher conversion of raw materials, higher product selectivity, high, improvement in energy efficiency, less use of fuels, use of benign solvents, substitution of raw materials with the renewable feedstocks, low amounts and less hazardous waste production, and lower secondary emissions [3]. In summary, green engineering needs to consider sustainability during process design.

At this point, it is necessary to consider sustainability and green engineering measures of processes. For this purpose, metrics on environment, economics and society seems reasonable. Environmental indicators of sustainability can be summarized as material & energy intensity, water consumption, toxic and pollutant emissions [9]. Economical indicators are related with profit, value and investments. Social indicators reflect attitudes toward employers, suppliers and customers [10].

Although it is more clear which concepts are to be considered in evaluating sustainability and green nature of existing facilities, it is harder to select and apply

process performance criteria to evaluate sustainability and environmental behavior of processes during process development.

This study aims at developing a methodology for the selection of process performance criteria that is applicable during process development incorporating environmental concerns into process design stages. Sustainability and green engineering concepts are the two concepts that are considered throughout the analysis.

From the sustainability point of view, the renewable raw materials should be considered. The use of petroleum-based feedstocks is no longer appropriate because of the depletion of reserves and the high price of petroleum [11]. Additionally, the extraction of crude petroleum and its processing to obtain functional groups causes additional impact on the environment [2]. Due to these reasons, interest in alternative, bio-based feedstocks, which can replace petroleum based feedstocks has increased. Biochemical feedstocks vary from sugar cane, sugar beet, corn, and the shells of almonds, hazelnut and walnut. Because the Earth's biomass is mostly ligno-cellulosic comprising agricultural and forestry wastes, the research is focused on cellulose conversion [2]. Cellulose of the feedstocks can be converted to preferably five or six carbon sugars using cellulase enzyme as the catalyst for the hydrolysis of cellulose. The five and six carbon sugars are utilized for further conversions and finally for the desired chemicals. Therefore, in this study alternative production pathways start from sugar-based raw materials and their conversion to the most promising 12 building blocks and finally to the desired products are examined for sustainable production. In fact, the source of inspiration for the selection of building blocks is a report prepared by the Biomass Program of the U.S. Department of Energy, Top-Value Added Chemicals from Biomass. The report identifies the screening results for the building block candidates selected due to chemical functionality and potential use. Twelve building blocks are considered for conversion to the intermediate chemicals to provide the industrial products and goods. In this study, the performance evaluation of processes based on the selected twelve building blocks to the intermediates is carried out in order to determine the most promising process routes for the development of a sustainable chemicals industry.

In the utilization of green engineering, process development is considered to be accomplished in three stages: conceptual design stage, preliminary design stage and fully developed design stage. In general, the common end-of-pipe approach is utilized to examine the environmental impact of fully-developed processes. The criteria which are applied at this stage consider the effects of the processes using indexes for global warming potential, stratospheric ozone depletion, acid deposition, smog formation and indexes related with the health related toxicity and carcinogenity [13]. On the other hand with sustainability indicators, the environmental performances of the processes can be evaluated at the preliminary design stage. However, neither the indexes for fully-developed processes nor those for preliminary designs are applicable at the initial conceptual design stage. Therefore, it is more difficult to utilize the usual environmental performance indicators at the conceptual design stage; for which the process information is composed only of the raw materials, the products and the conversion route. The most appropriate criteria at the conceptual design stage are selected as the persistence, bioaccumulation and toxicity of the chemicals involved, and the atom and mass efficiency and economical potential of the production routes [13]. The lack of property data for the evaluation of the environmental impact of the chemicals led to the use of the physical and chemical property estimation program EPISuite developed by the Environmental Protection Agency (EPA) of USA [12]. The results of EPISuite are utilized to assess the environmental performance of the bio-based and petroleum-based chemicals, and comparison of alternative routes. For the economical criteria evaluation the economical potential of the pathways are investigated. The atom and mass efficiency calculations are completed utilizing the reaction stoichiometries of the production pathways. In addition to these, the relationship between the free energies of reactions and the economical potential of the routes are investigated to determine its usability as a further criterion at the conceptual design stage.

One of the many products is selected for further investigation of the conceptual design and the construction of the preliminary design. For this purpose 1,3 propanediol, is selected which is given a high importance by many leading companies for its potential of replacing nylon. The preliminary design stage criteria which are accepted as the sustainability metrics are applied to the newly proposed production routes of 1,3

propanediol with *Klebsiella pneumoniae* (DSM 2026) and *Clostridium butyricum* (F2b) strains.

CHAPTER 2

LITERATURE SURVEY

Environmental concerns, regulations and restrictions bring about two important concepts namely, sustainability and green production of the commercial organic chemicals. The sustainability part focuses on the substitution of renewable feedstocks instead of conventional raw materials. The green production part is related with the incorporation of environmental concerns into the design stages in order to minimize the environmental impact of the production routes.

Production of well-known organic chemicals with conventional synthesis routes can be replaced by novel processes with sugar based feedstocks. The U.S. Department of Energy in the context of its Biomass Program has considered these new routes. First their report on this topic will be presented in this Chapter Section 2.1.

In the second section of this chapter literature on selection and utilization of process performance criteria during the design stage to evaluate the environmental impact of the processes will be reported.

2.1 Top-Value Added Chemicals from Biomass Volume I- Results of Screening for Potential Candidates from Sugars and Synthesis Gas [1]

Screening results for potential candidate molecules from sugar- based biomass feedstocks to value added chemicals were presented in this report. The report was prepared by the Biomass Program of U.S. Department of Energy, which supports the development of new technologies to use domestic and sustainable resources from plants to increase energy supply of USA. To succeed in these aims, the Program explores and suggests a processing facility to convert biomass into multiple products, like fuels and high value chemicals.

The report identifies the most promising twelve building blocks from sugar-based biomass, the intermediates obtained from the building blocks and products which are produced from the intermediates. The selection of the most promising candidates is done by considering petrochemical raw materials and their desired products. Then, alternative production routes for the same chemicals are developed with the biomass-based feedstocks. Analogous models for both types of feedstocks are represented in Figures A.1 & A.2 [13]. The down selection of the twelve most promising bio-based building blocks depends on several criteria; which are:

- The cost of raw materials
- Estimated processing costs
- Estimated market price of the products
- Technical complexity of the production routes
- Market potential of each candidate

Considering the listed criteria, 50 candidate building blocks are then categorized considering the functional groups of the building blocks and their potential uses. The reason why the chemical functionality is used as a parameter is that the more functional groups a candidate possess a high number of potential downstream products exists. Also, the possibility of production from starch and/or lignocellulosic feedstocks, and being already a commercial product are considered as further screening criteria. The 'most promising building blocks' are presented in Table 2.1.

The conversion of sugars into the twelve building blocks is presumed to be achieved via fermentation by aerobic microorganisms. The conversion of building blocks to products is to be achieved by one or more steps involving reduction, oxidation, dehydration, bond cleavage and polymerization. Biochemical conversion of the building blocks into the products is taught to be achieved mainly by enzymatic reactions.

Table 2.1 The Top 12 Sugar- Derived Building Blocks [1]

Building Blocks		
Glycerol	Aspartic Acid	Itaconic Acid
Sorbitol	Glucaric Acid	Levulinic Acid
Xylitol/Arabinitol	Glutamic Acid	3- Hydroxybutyrolactone
1,4 Diacids (Succinic, Malic and Fumaric)	2,5 Furan Dicarboxylic Acid (2,5 FDCA)	3- Hydroxypropionic Acid

Products considered to be produced starting with the twelve building blocks are provided in the following table. The structures of the building blocks, the biochemical and petrochemical production routes of the products which are reported in the literature are presented in Appendix A.2 & A.3. Products which are considered in this study are shown in Table 2.2.

Table 2.2 The Derivatives of the Twelve Building Blocks

Derivative Name			
Acrylonitrile	2,5 Dihydroxymethyl Furan	2-Amino-3 Hydroxy THF	2,5 Dihydroxymethyl THF
Acrylic Acid	Diphenolic Acid	G-Butenyl Lactone	Prolinol
Angelilactones	DBE	Acrylamide	1,3 Propanediol
Ethyl-3HP	Epoxy Lactone	Itaconic Diamide	Pyroglutamic Acid
Lactic Acid	Glycerol Carbonate	Malonic Acid	Succindiamide
Glycerol	Glutaric Acid	Norvoline	Tetrahydrofuran
Glutaminol	G-Valerolactone	Propylene Glycol	Succinic Acid

Table 2.2 (cont'd) The Derivatives of the Twelve Building Blocks

Derivative Name			
Aspartic Anhydride	Ethylene Glycol	α-ketoglucarates	3-Methyl Pyrrolidone
Pyroglutaminol	G-Butyrolactone	3-&4- Methyl NMP	1,4 Sorbitan
Amino-2-Pyrrolidone	Mixture of Hydroxyfurans	Amino-γ-Butyrolactone	5-Amino-1-Butanol
Acrylate Lactone	Glyceric Acid	Methyl Acrylate	Succinonitrile
B-Acetylacrylic Acid	2-Amino-1,4 Butanediol	2-methyl-1,4 Butanediamine	2-methyl-1,4 Butanediol
2-Pyrrolidone	Glucaro-γ-lactone	Propanol NMP	3-Hydroxy-THF
D-Aminolevulinate	Glucarodilactone	Propiolactone	3-Methyl THF
1,5 Pentanediol	Glucaro-δ-lactone	1,4 Pentanediol	2-Methyl-THF
2,5 Furan Dicarbaldehyde	2,5 bis-(Aminomethyl) THF	2,5 Anhydrosugars	1,4 Diaminobutane
3-Amino-THF	Xylaric Acid	3-&4- methyl GBL	Proline

The products listed in Table 2.2 are considered to be produced from petrochemical raw materials as well as from the biological feedstocks. The commercial production routes for the products reported in the literature are summarized in Appendix A.4.

2.2 Process Performance Criteria

Chemical process design can be examined in three stages. It starts with the conceptual design stage. This stage is followed with the preliminary design stage. Finally, if a process is promising as cost-effective and environmentally friendly, then a fully developed process design is worked out [13]. Conventional design methods

examine the environmental impacts of processes when the process is fully specified. The results obtained with this approach are sub-optimal in relation to the environment, since the process performance is also dependent on the structure and design conditions. Therefore, in order to improve environmental performance, environmental impact of the processes should be considered and minimized at an early design stage. Environmental impact minimization concerns should be followed throughout the development stages of the process design.

The evaluation of environmental impacts of processes is performed considering different environmental measures or indexes. The measures, indicators and indexes for environmental performance evaluations reported in the literature are summarized as stage 1, 2, 3 criteria in Tables 2.3 to 2.6 considering three design stages, namely conceptual, preliminary and fully developed design stages. In Table 2.3, the performance criteria for conceptual design stage are reported.

Table 2.3 Environmental Performance Criteria at the Conceptual Design Stage

Criterion	Description
Atom Efficiency	Proportion of atoms in raw materials appearing in the final product [8]
Bioaccumulation- Based Methods	Take into account bioaccumulation in food chain[7]
Environmental Index (EI)	EI= 1 / TLV [13]
Environmental Index (EI)	EI = $\sum \lvert \upsilon_i \rvert x$ (maximum of oral and inhalation weighting factor) [13]
Mass Efficiency	Ratio of the mass converted to the desired product to the mass of reactants [13]
Persistence	Stability of a chemical in any compartment of the environment for a period of time[13]
Toxicity	Concentration level of a substance that starts to become harmful to living organisms [13]

The criteria at the conceptual design stage should be when the elementary data on raw materials, products and processing routes are available. At this stage, the input-

output structure of the processes is known or can be easily constructed. Therefore, criteria for comparison of processes should be easy, simple and restricted with the input-output structure. Persistence, bioaccumulation, toxicity, atom and mass efficiencies are the criteria at the conceptual design stage. The environmental indexes provided in the table are used for toxicity evaluations. The toxicity criterion listed in Table 2.3 needs additional definitions to evaluate the effects of the chemicals. These are listed in Table 2.4.

The preliminary design stage criteria for environmental performance evaluation are provided in Table 2.5.

At the preliminary design stage, the design basis, process equipment, emissions and wastes can be known or calculated using material and energy balances. Therefore, the second stage criteria include the material & energy consumption values together with the release quantification of toxics and pollutants.

At the fully-developed design stage, since all process information is available, the possible environmental performance criteria are higher in number. The criteria that could be utilized at this third and final stage are presented in Table 2.6.

Table 2.4 Toxicity Assessment Definitions Used in the Evaluation of Toxic Effects of Chemicals

Toxicity	• Threshold Limit Values (TLVs) [13] • Permissible Exposure Limits(PELs) [13] • Recommended Exposure Limits(RELs)[13] • The oral reference dose, cancer potency[7] • Reference Dose (RfD) [14] • Inhalation Reference Concentration (RfC)[14]

Table 2.4 (cont'd) Toxicity Assessment Definitions Used in the Evaluation of Toxic Effects of Chemicals

Toxicity	• No Observable Adverse Effect Level (NOAEL) [14] • Lowest Observable Adverse Effect Level(LOAEL)[14] • LC_{50}(Median lethal concentration for inhalation) [15] • LD_{50}(Actual lethal dose to evaluate toxicity by other routes namely oral, intraperitoneal, intravenous for rats or mice)[15] • EC_{50}(The concentration at which other effects are observed rather than death of organisms)[16] • ChV(effect of a chemical staying in the life-span of the microorganism when the organisms are exposed to long-term exposure)[17] • Oral slope factor(risk of a chemical to some dose when it is ingested)[18] • Unit risk (upper bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 microgram/L in water and 1 microgram/ cubic meter in air)[18]

Table 2.5 Environmental Performance Criteria at the Preliminary Design Stage

Measure	Description
Energy Intensity	Net Energy Consumed in Primary Fuel Equivalents / Output [19]

Table 2.5 (cont'd) Environmental Performance Criteria at the Preliminary Design Stage

Material Intensity	Mass of Raw Materials – Mass of Products / Output [9 &19]
Pollutant Effects	Measure of Pollutant Effect/ Output [9&19]
Toxic Release	Mass of RecognizedToxics / Output [9&19]
Water Consumption	Volume of Fresh Water Consumed / Output [9&19]

Table 2.6 Environmental Performance Criteria at the Fully-Developed Design Stage

Measure	**Description**
Acidification Potential (AP)	Contributions of SO_2, NO_X, HCl, NH_3, HF to potential acid deposition [8]
Best Practicable Environmental Option (BPEO Index)	Contribution of process release to concentrates at receptor; one index value is calculated for each release into each medium [8]
Biological Oxygen Demand (BOD)	Measure of organics in water, expressed as demand of oxygen for degradation of the organics present in water [8]
Burden/Impact Factor	Contribution of process release to defined harm category such as global warming, ozone depletion etc. [8]
Critical Air Mass(CTAM) (kg air/h)	Mass of air emissions (kg pollutant/h)/ standard limit value (kg pollutant/kg air) [8]
Critical Water Mass(CTWM) (kg water/h)	Mass of water pollutant (kg pollutant/h)/ standard limit value (kg pollutant/kg water) [8]
Ecological Risk (ER)	Concentration of contaminant at specificed location exposed to ecological community population/reference dose[20]

Table 2.6 (cont'd) Environmental Performance Criteria at the Fully-Developed Design Stage

Measure	Description
Environmental Load Factor (ELF)	ELF = (Weight of waste)/ (Weight of the product) [8]
Environmental Quantity Standard	Acceptable concentration of material in the environment leading to negligible harm [8]
Environmental Impact Matrix	Pollutant-by-pollutant comparison of mass releases[21]
Eutrofication (Nutrification) Potential	Potential to cause over-fertilization of water and soil. Emissions of NO_X, NH_4^+, N, PO_4^{3-}, P are responsible for eutification [8]
Global Warming Impact (GWI) (kg CO_2/h)	GWI = Mass of pollutant (kg/h) x GWP (kg CO_2 /kg pollutant) [8]
Ozone Depletion Potential (ODP)	Ozone depletion of a substance relative to the ozone-depletion potential of CFC-11 [8]
Potential Chemical Risk(PCR)	Potential risk to human health associated with the manipulation, storage and use of hazardous chemical compounds in the process [22]
Potential Environmental Impact(PEI)	Potential impact to environment due to the emissions and the discharge of the hazardous chemicals to the environment[22]
Release Concentration	Concentration of the pollutant at defined location [8]
Resource Depletion (RD)	Depletion of non-renewable resources (fossil fuels, metals, minerals) [8]
Safety Risk (SR)	Individual risk factor at the study area due to any eventuality in operation[20]
Weighted Waste Measure	Overall Index = Sum of(Release Rate x Harm Factor of Each Substance) [8]
Smog Formation Potential (SFP)	Smog formation is related with the ozone layer formed via photochemical reactions involving hydrocarbons and NO_X[13]

Table 2.6 (cont'd) Environmental Performance Criteria at the Fully-Developed Design Stage

Measure	Description
Solid Mass Disposal(SMD) (kg solids/h)	Mass of Solid Wastes(kg pollutant /h)/ Standard limit value (kg pollutant/ kg waste) [8]
Sustainable Process Index(SPI)	Calculation of the area (raw materials area, energy supply area, infrastructure area, staff area, product dissipation area) required to sustainingly embed a process into an environment[23]
Waste Ratio	Waste ratio = Waste/All products x 100% [8]

The utilization of third stage criteria requires a detailed flowsheet and extensive data on the processes. Frequently, such data exists only for already operating plants.

The listed environmental performance indicators could be utilized during process design. Most of the indexes are appropriate to use at the fully developed process design stage. Indexes or measures which are selected to be used in this study are provided in the methodology section.

The next sub-section contains the literature information on 1,3 propanediol production processes utilizing commercial and novel routes. In this study, second stage criteria are applied to 1,3 propanediol production from glycerol.

2.3 1,3 Propanediol Production by Commercial and Novel Routes

2.3.1 Background on 1,3 Propanediol Production

1,3 propanediol has been known as a fermentation product since 1881 by identification of August Freund. Although it was discovered over a century ago, little attention was paid to that chemical until 1995. In fact, its price was very high to compete with other diols. Therefore, its use and market volume was small. In 1995, the market

for 1,3 propanediol changed with the new polyester technology developed by Shell Chemical Company. The new polyester is suitable for fiber and textile applications and is composed of terephthalic acid and 1,3 propanediol by a reaction of ethylene oxide, carbon monoxide and hydrogen. Another route was developed by Degussa in Germany. The production process of Degussa is the hydrolysis of acrolein. Degussa's sythesis route has been taken up by DuPont. The strategy of DuPont is also try to utilize glycerol and glucose for 1,3 propanediol production [24]. The reason DuPont gives so much importance to 1,3 propanediol production is that DuPont expects that 1,3 propanediol will eventually replace nylon [25].

Since there is much attention in the newly developed routes for 1,3 propanediol production and due to its potential for various purposes and products, it is considered in this study to investigate its production at the preliminary design stage.

2.3.2 1,3 Propanediol Production from Glycerol by Fermentation

The biotechnological synthesis of 1,3 propanediol (PDO) can be achieved by utilization of glycerol as a substrate, direct fermentation of sugars or utilization of sugars and glycerol as co-substrates using different strains.

The major biotechnological production of PDO is the fermentation of glycerol under anaerobic conditions. The raw material glycerol is produced from fat saponification. However, the formation of glycerol as a by-product in the biodiesel production increases the market volume of glycerol since, the transesterification of any vegetable oil produces 90 wt% fatty acid methyl esters (biodiesel) and 10 wt% crude glycerol [26].

Glycerol can be converted to value added products. It can be converted to 1,3 propanediol, acetic acid, 2-3 butanediol, ethanol and lactic acid by facultative anaerobic bacteria. However, the most promising product among the possible products is 1,3 propanediol. The reason is the use of this glycol as a monomer in polyester and polyurethane synthesis. Moreover, plastics produced from 1,3 propanediol show better properties and higher light stability than plastics produced from 1,2 propanediol,

butanediol or ethylene glycol. Also, 1,3 propanediol is used as a polyglycol-type lubricant and a solvent[26].

The conversion of glycerol to 1,3 propanediol in significant amounts is provided by several bacterial strains. The strains include *Citrobacter, Klebsiella*, *Clostridum* and *Lactobacillus* [27]. The utilization of different strains provides the comparison of processes in terms of productivity, yield and cost of operation. For instance, Klebsiella strain can utilize only pure glycerol; whereas the newly developed Clostridum strains can utilize both raw and pure glycerol. *Klebsiella pneumoniae* utilizes only pure glycerol because with this strain, the salts produced due to transesterification of oil causes inhibition on the cell growth, whereas *Clostridium butyricum* strains are not affected by the use of industrial glycerol [26].

The selection of microorganism type and the differing characteristics of the processes are provided in the methodology section.

CHAPTER 3

METHODOLOGY

In this part of the study, the approach which is utilized for the selection and application of the criteria at the conceptual design stage, so called “stage 1”, and at the preliminary design stage called as “stage 2” are described in detail. In general, the applied methodology for the environmental performance evaluation of chemicals is a modification of the criteria considered in Allen & Shonnard [13]. The first stage criteria are selected as environmental criteria composed of persistence, bioaccumulation and toxicity potentials of the chemicals, together with economical potential evaluation, atom & mass efficiencies of the processes and Gibbs free energy versus economical potential relationship. As the second stage criteria, material & energy consumption of the processes, water consumption and emissions of the gases to the atmosphere are selected as the preliminary design stage environmental criteria. The second stage criteria is applied to 1,3 propanediol production processes.

The analysis which is considered in the first stage is shown in the following three figures. The first figure summarizes the approach that is followed to assess the environmental performance of processes at the first design stage. Here, initially, it is required to obtain the physical and chemical properties which are needed to evaluate persistence, bioaccumulation and aquatic toxicity of the chemicals. The physical and chemical properties can be provided by using the software programs. Because the chemicals considered in this study are novel, the experimental values of the needed physical and chemical properties are not reported in the literature. Both of the property estimation programs are developed by U.S. Environmental Protection Agency (EPA) and updated regularly. EPISuite is freely downloadable from EPA’s webpage. There are thirteen sub-programs and three fate estimation models in the EPISuite. Among these sub-programs included in EPISuite, AOPWIN, BCFWIN, BIOWIN and ECOSAR are

the programs utilized in the first stage environmental performance evaluation. The estimation equations included in these programs are developed using available experimental values of the desired property for different number of chemicals and fragment contributions of similar functional groups of the chemicals. PBT Profiler is available for public use on its webpage and helps industry to screen alternatives. The program gives information about persistence, bioaccumulation and chronic fish toxicity of the chemicals and the release scenarios for the chemical in concern. Unfortunately, both of the estimation programs are limited and can not estimate the properties for inorganic chemicals, organic salts, high molecular weight compounds, chemicals with unknown or variable composition, mixtures, surfactants, highly fluorinated compounds. The results of EPISuite and PBT Profiler together with the ranges provided by the estimated properties give the opportunity to evaluate the environmental performance criteria.

Stage 1 Criteria for economic analysis, atom & mass efficiency calculations and the relationship between the economical potential and the Gibbs free energy of reactions are presented in Figure 3.2. Basically, economical analysis depends on the product revenue, raw material costs and the reaction stoichiometry. The conversion of atoms or mass of raw material to products is calculated for conventional and novel production of chemicals with the aim of determining the attractiveness of processes. Additionally, the economical potential versus Gibbs free energy relationship is examined considering the effect of spontaneity of the reactions. Application of the second stage criteria is described in Section 2.7.

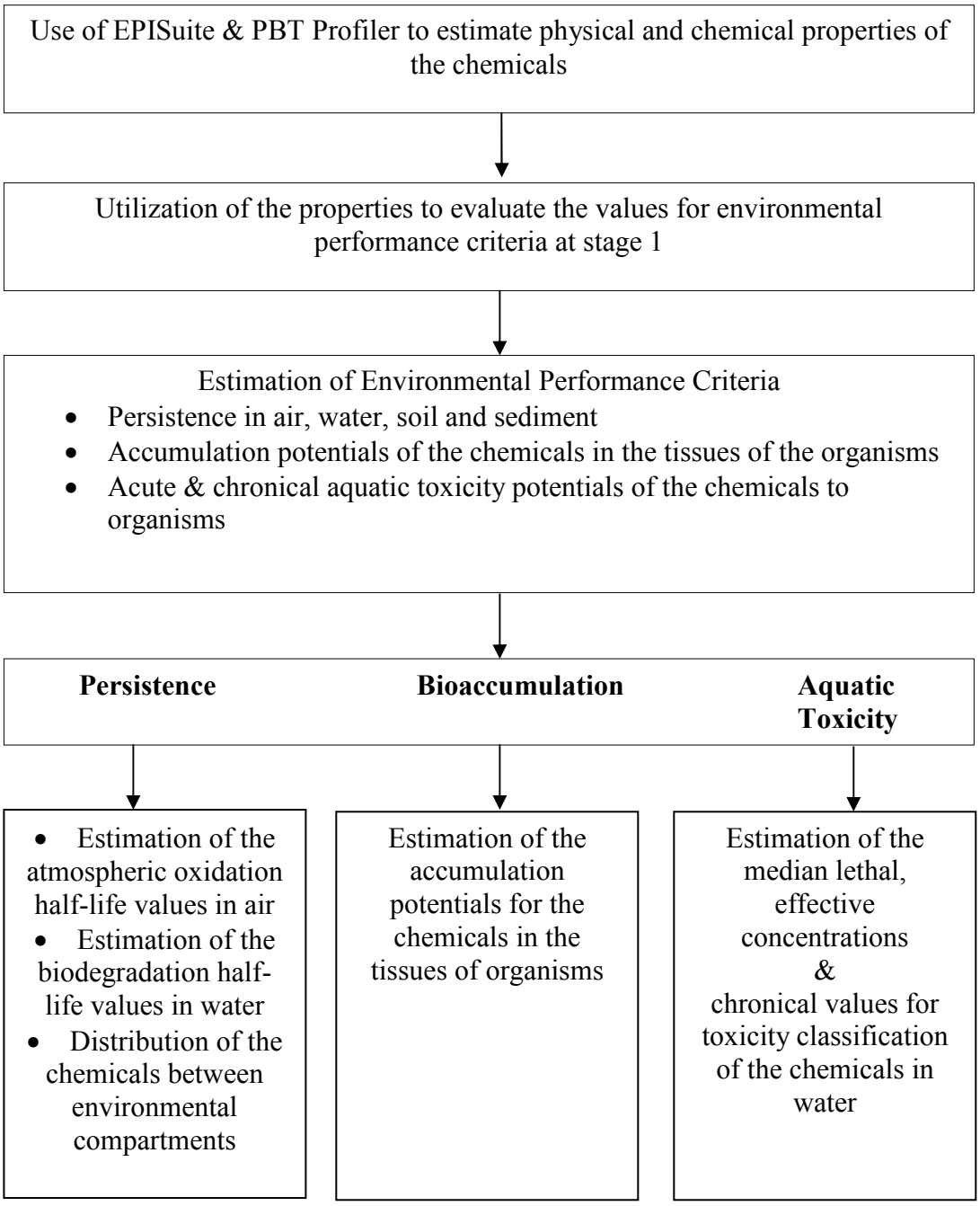

Figure 3.1 The Approach Used in Estimating Environmental Criteria for Stage1

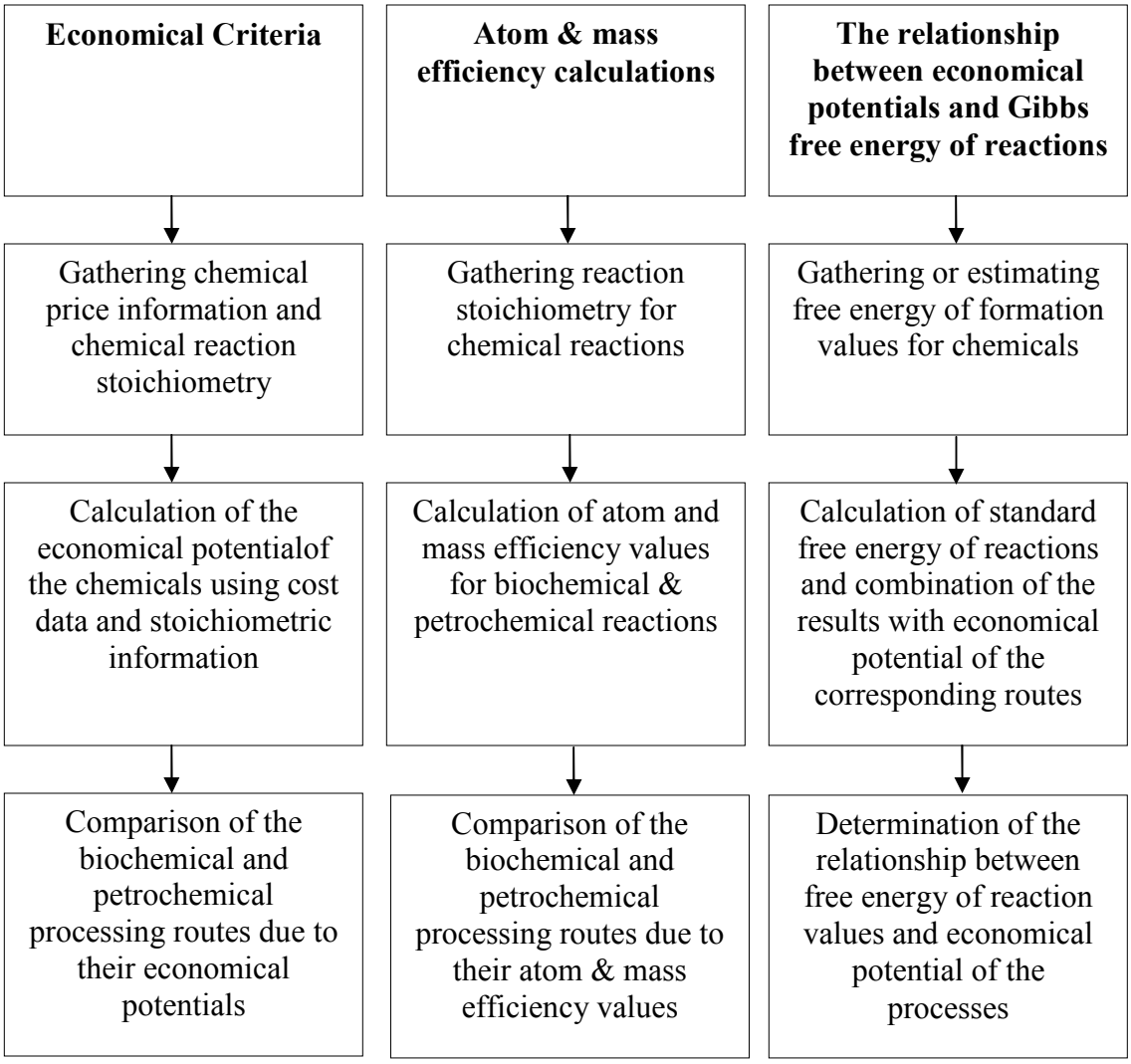

Figure 3.2 The Approach Used to Evaluate Economic Potential, Atom and Mass Efficiency and the Relationship Between Free Energy of Reactions & the Economic Potentials of Processes at the Conceptual Design Stage

The approach for persistence, bioaccumulation and toxicity evaluation is explained in detail in the following sub-sections.

3.1 Evaluation of the Persistence of Chemicals

First criterion in the environmental performance evaluation at the conceptual design stage is the persistence of chemicals. The approach in determining persistence of the chemicals is considered in two environmental compartments: persistence in air and water. Persistence estimations are combined with a multi-media model which examines the partitioning of a released chemical in different environmental media. Persistence evaluation is first explained for air, which is described in the following figure.

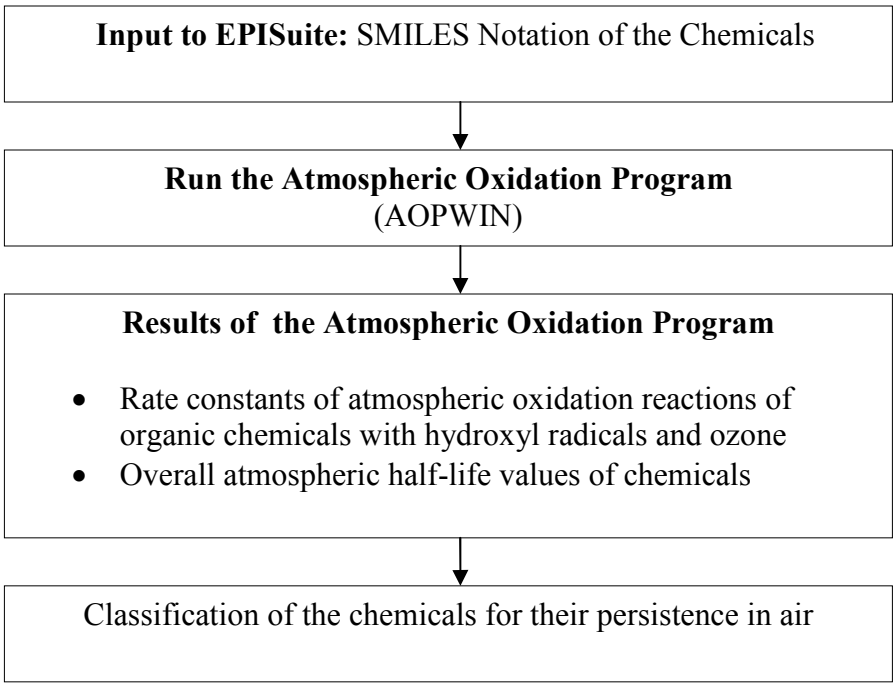

Figure 3.3 The Approach Used to Determine the Persistence of a Chemical in Air

Persistence evaluation of the chemicals starts with entering the SMILES (Simplified Molecular Input Line Entry System) notations of the bio-based and petroleum-based raw materials and the products to into EPISuite. The detailed information about the SMILES notation is given in Appendix B.1. For this purpose,

atmospheric oxidation rate program is used to evaluate persistence in air. Experimental rate-constants are used by the program if the values are available in the database. If not they are estimated by the Atmospheric Oxidation Program (AOPWIN). AOPWIN is accurate for hydroxyl radical reaction rate estimations considering 667 compounds with an absolute mean error of 0.127 and for ozone reaction rate estimations with 112 organic chemicals, the absolute mean error is 0.35 in comparison with experimental values [12]. The rate constants are converted to half-life values by the program utilizing the equations given below. The two software programs (EPISuite and PBT Profiler) use the same reaction rate constants to evaluate the half-life values, but they differ in the assumption of hydroxyl radical and ozone concentration in air. AOPWIN uses 12-hour day basis with a hydroxyl concentration of $1.5x10^6$molecules/cm^3 [12] and PBT Profiler uses 24-hour day basis and with a concentration of $5x10^5$molecules/cm^3. Both of the programs estimate the half-life for ozone reaction similarly. The equations for half-life calculations in AOPWIN are given as follows [12]:

Hydroxyl Radicals Half-life: 0.693/ (rate constant cm^3/molecule-sec x $1.5x10^6$ molecules/cm^3x 43200 sec/day) (3.1)

Ozone Half-life: 0.693/ (rate constant cm^3/molecule-sec $x7x10^{11}$ molecules/cm^3 x 43200 sec/day) (3.2)

1/ Overall Half-life: 1/ Hydroxyl Radicals half-life + 1/ Ozone half-life (3.3)

When the overall half-life in air is estimated using the above equations, persistence of the chemical in air is classified as having higher or lower than a half-life value of 2 days. If the half-life value is less than 2 days, the chemical is considered as not persistent and if the half-life value is greater than 2 days, then the chemical is considered to be highly persistent. This classification for persistence of the chemicals is provided in Table 3.2 together with the persistence classification of chemicals in other compartments.

The persistence of organic chemicals in water is estimated by the biodegradation probability program (BIOWIN). BIOWIN is composed of six different types of sub-programs and gives biodegradation probabilities for linear, non-linear models and

primary, ultimate biodegradation estimations. BIOWIN 3- expert survey ultimate biodegradation model is used for determination of persistence in water. Because this model includes the transformation of a chemical to carbon dioxide and water rather than initial metabolites and the indexes for biodegradation can be converted to time requirement for biodegradation, this model is selected for the evaluation of persistence in water. The model depends on a survey of 17 U.S. EPA biodegradation experts evaluated 200 chemicals to achieve the required time for ultimate and primary biodegradation [12].

The overall approach to determine the persistence of the chemicals in water is described in the Figure 3.4.

The persistence of chemicals in water is determined using a similar approach to the persistence in air. The BIOWIN program gives six different types of model results as the output. The ultimate biodegradation probability model predicts a biodegradation index which is rated from 1.0 to 5.0 which in turn is converted to half-life values by assigning certain periods to certain time-frames [12]. The rating index, time-frame and half-life conversions are presented in Table 3.1.

In Table 3.1, it is observed that the maximum value for the half-life of a chemical in water is set as 180 days although the half-life of recalcitrant molecules is longer than this set value. However, during the program development, it is determined that use of longer half-life value did not affect the results [12]. The half-life values are used to classify the chemicals due to the criteria summarized in Table 3.2.

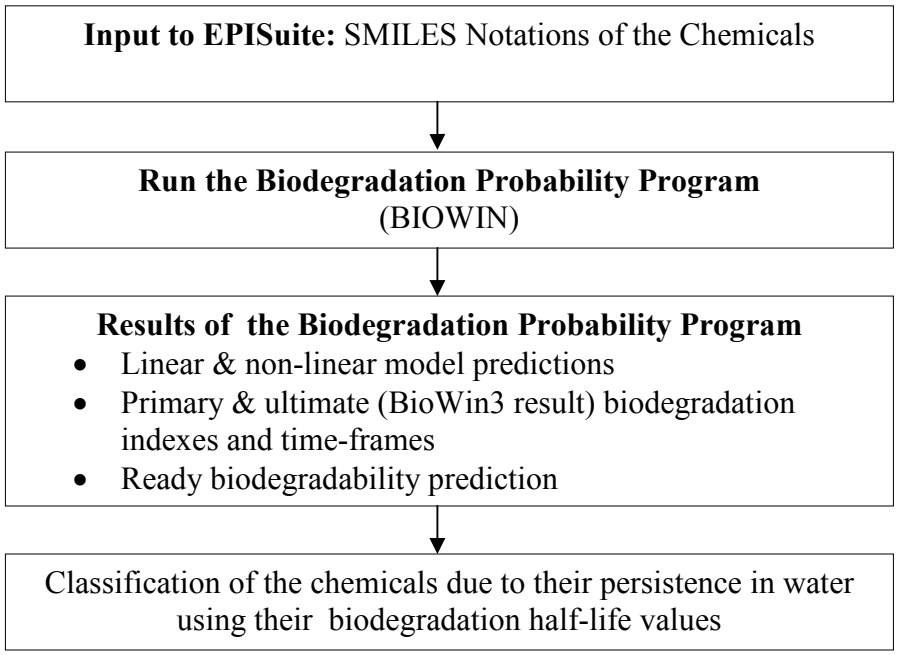

Figure 3.4 The Approach Used to Determine Persistence of a Chemical in Water

Table 3.1 Rating of the BioWın-3 Output Values and Their Conversion to Half-life Values in Water

Biodegradation Index Rated by the program	Time Required for Biodegradation	Converted Assigned Half-Life (days)
5.0	Hours	0.17
4.5	Hours to days	1.25
4.0	Days	2.33
3.5	Days to weeks	8.67
3.0	Weeks	15
2.5	Weeks to months	37.5
2.0	Months	60
1.0	Longer	180

Estimations of persistence in soil and sediment media are obtained by the utilization of BIOWIN-3. Ultimate biodegradation is slower under anaerobic conditions than aerobic conditions and it is assumed that the rate of ultimate biodegradation in sediment is assumed as on the average one-ninth (1/9) of that in water. In a similar manner, the biodegradation rate for a chemical in soil approximately one-half (1/2) that in water. Therefore, half-life in sediment is 9 times the half-life in water and the half-life in soil is twice that estimated for water [29].

Table 3.2 Persistence Criteria in PBT Profiler [28]

Environmental Compartment	**Half – Life (days)**		
	Not Persistent	**Persistent**	**Highly Persistent**
Water	< 2 months	≥ 2 months	> 6 months
Soil	< 2 months	≥ 2 months	> 6 months
Air	≤ 2 days		> 2 days
Sediment	< 2 months	≥ 2 months	> 6 months

Once the persistence in air and water are determined, the partitioning of a chemical in the four media when it is released to the environment is considered. Basically, the partitioning of a chemical in any compartment and its life-time in this specific medium determines the degradation of this chemical in the environment. The distribution of a released chemical in different environmental compartments is determined by the use of a multimedia compartment model developed for this purpose.

The level-III multimedia mass balance model or fugacity model developed by Mackay and co-workers predicts chemical concentrations in several environmental compartments simultaneously. The model is advantageous in the sense that it is computationally efficient and includes transport mechanisms between compartments and degradation[12]. This model is included as a sub-program in EPISuite but it is run with EPIWIN (a sub-program of EPISuite, which gives the summary of the all sub-programs

and results of the programs, only operates with the run of EPIWIN). It is significant here to discuss the features, input properties and assumptions of the model.

The Mackay Level-III fugacity model is "a non-equilibrium and steady-state model developed to provide information about the partitioning in environment and inter-media transport at the process screening level" [29].

The steady-state concentrations of each chemical in the environmental compartments in comparison with a constant emission into a defined volume of environmental region are predicted by the model utilizing the physical and chemical properties of a chemical [13]. The physical and chemical properties are used to determine the transport between the environmental compartments. The utilized properties are provided below which are estimated by sub-programs of EPISuite when there is lack of property information:

- Henry's Law Constant
- Vapor Pressure
- Melting Point
- Octanol /water partition coefficient
- Molecular weight
- Water solubility

All of these properties are estimated at 25 ˚C. Although the temperature of different environmental media may vary from this value, estimations at this temperature will provide an insight for screening purposes.

The estimation programs considering level-III fugacity model are run using default-settings. The values are for emission rates to the compartments and the size of the environment. The emission rates are set as either 0 or 1000 kg/h for soil, water and air, with the assumption that there is no direct discharge to the sediment. The size of the environment is represented with an environment having the size of the Ohio state [29]:

- Surface: 100,000 km^2 containing 10% water; 90% soil surface
- Water depth: 20m
- Soil depth: 20 cm
- Sediment depth: 5 cm
- Atmospheric height: 1000m (typical height affected by pollutants emitted at the Earth's surface)

Chemicals may enter to the compartments either by emissions or advective mechanisms. Transfer of chemicals between environmental compartments by diffusive and non-diffusive processes characterized by intermediate transfer values. Additionally, multi-media compartmental model uses the fugacity concept for mass transfer and reaction within chemical compartments. Partitioning of a chemical between environmental phases is described by the equilibrium criterion of equal fugacity in all phases [13].

Together with the biodegradation half-lives and Level-III fugacity model results are evaluated to determine the persistence of a chemical in certain environment. This determination is made due to the results obtained from the PBT Profiler, although the EPISuite runs with the same logic and uses a similar methodology. The reason for choosing the PBT Profiler is that the classification of chemicals with the PBT Profiler results is available in the literature.

3.2 Evaluation of the Bioaccumulation Potentials of Chemicals

The accumulation of the chemicals in the fatty tissues of organisms is determined by using either EPISuite or PBT Profiler. In EPISuite, bioconcentration factor or octanol-water partition coefficient estimation programs can be used. PBT Profiler also uses bioconcentration factor method giving the same results with those of EPISuite. The approach that is followed for bioaccumulation classification of the chemicals is summarized in Figure 3.5.

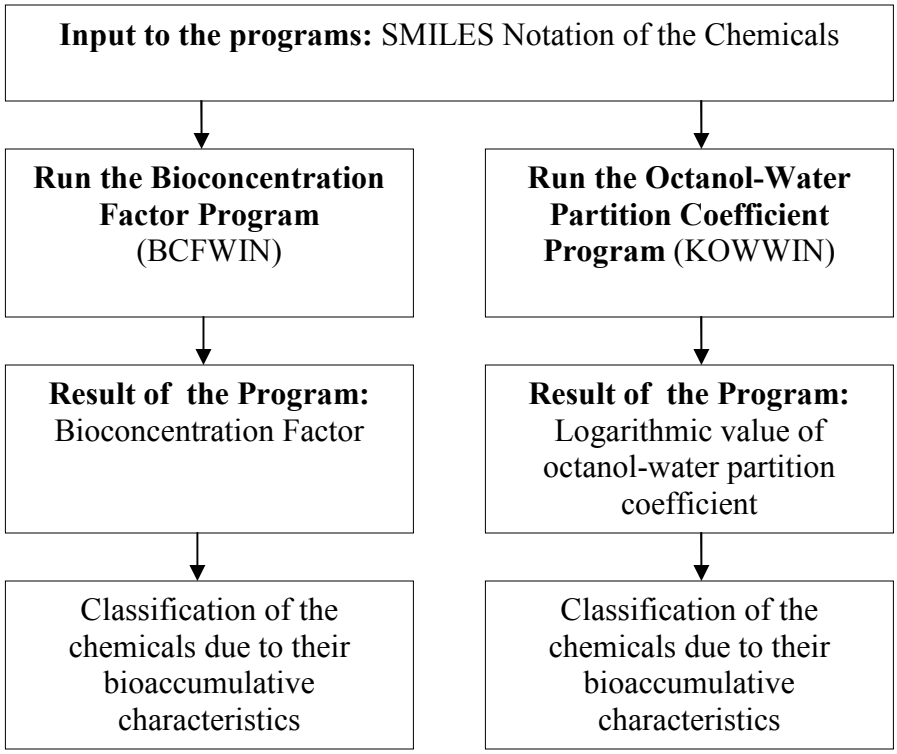

Figure 3.5 The Approach Used to Determine Accumulation of the Chemicals in the Tissues of the Organisms

It is important to clarify the definitions and physical meanings of bioconcentration factor (BCF) and octanol-water partition coefficient (K_{OW}). The bioconcentration factor is the 'ratio of a chemical's concentration in the tissue of an aquatic organism to its concentration in water and indicated the accumulation of the chemical in the food chain'. Similarly, octanol-water partition coefficient is the 'equilibrium ratio of the concentration of a compound in octanol (lipophilic phase) to its concentration in water (hydrophilic phase)' and is significant for the partitioning between the hydrophilic and hydrophobic phases in the environment and human body [13]. Hence, both of these properties determine the accumulative characteristics of chemicals in the organisms. Octanol- Water Partition Coefficient Program uses Atom/Fragment Contribution (AFC) method. Coefficients for individual fragments and groups in KOWWIN were constructed by utilizing multiple regressions of measured

values for more than 2400 chemicals.The mean error is approximately 0.161[12]. Description of Bioconcentration Factor Estimation Program is given in Appendix B.2.

The classification criteria of EPISuite are different from that of PBT Profiler. In Table 3.3, the limits for bioaccumulative behavior of the chemicals in PBT Profiler are provided.

Table 3.3 Bioaccumulation Classification for the PBT Profiler [28]

No Regulatory Concern	Bioaccumulative	Highly Bioaccumulative
BCF < 1000	BCF ≥ 1000	BCF ≥ 5000

Although a bioconcentration factor value less than 1000 require no regulatory concern, a scale for the chemicals having a bioconcentration factor smaller than 1000 was developed [13]. This range for the bioconcentration factor and the logarithmic value of octanol-water partition coefficient is provided in Table 3.4 for both low and high ranges of the bioaccumulation potential. The range for bioaccumulation potential is rather restricted in Table 3.4.

Table 3.4 Bioaccumulation Classification for BCFWIN and KOWWIN [13]

Bioaccumulation Potential	Range for classification
High Potential	8.0> $\log K_{OW}$ >4.3 or BCF>1000
Moderate Potential	4.3> $\log K_{OW}$ >3.5 or1000 >BCF >250
Low Potential	3.5> $\log K_{OW}$ or 250>BCF

If environmental concerns for bioaccumulation become stricter, new scales can be developed particularly for the smaller ranges of the bioconcentration factor.

3.3 Evaluation of Toxicity of the Chemicals

Toxicity of the chemicals in aqueous media is estimated by the utilization of the Ecosystem Risk Program sub-program (ECOSAR) included of EPISuite. The overall approach is presented in Figure 3.6.

ECOSAR Class Program includes different SAR equations for different special group of chemicals. These "Special Classes" include (a) Polymers, (b) Inorganics, (c) Dyes, and (d) Surfactants. The current version of the ECOSAR Class Program does not include SARs for Polymers, Dyes, or Inorganics (these may be added in the future). However, SARs are available for various Anionic, Cationic, Nonionic, and Amphoteric Surfactants. All SARs are calculated from SMILES and log Kow values [12].

ECOSAR gives the median lethal and effect concentration & chronic concentration values for a chemical in the aquatic media for different exposure times for fish (both fresh and salt water), water fleas (daphnids) and green algae. On the other hand, PBT Profiler provides only the chronic value for fish. Therefore, the aquatic toxicity evaluation is performed using the EPISuite results.

As an example, the results of ECOSAR for glycerol are provided in Table 3.5. In this table, there are abbreviations such as LC50, EC50 and ChV for lethal concentration, effect concentration and chronic value. If an after short-lived exposure 50 % of a group of test organisms are expected to die, this concentration is called as LC50. If effects other than death are observed of it is called as EC50 [16]. Chronic value is the effect of a chemical during the life-span of an organism for a long-term exposure.

It is important to convert the concentration values reported in Table 3.5 to environmental concerns for the chemicals. This is achieved by taking into consideration information provided in Tables 3.6 & 3.7.

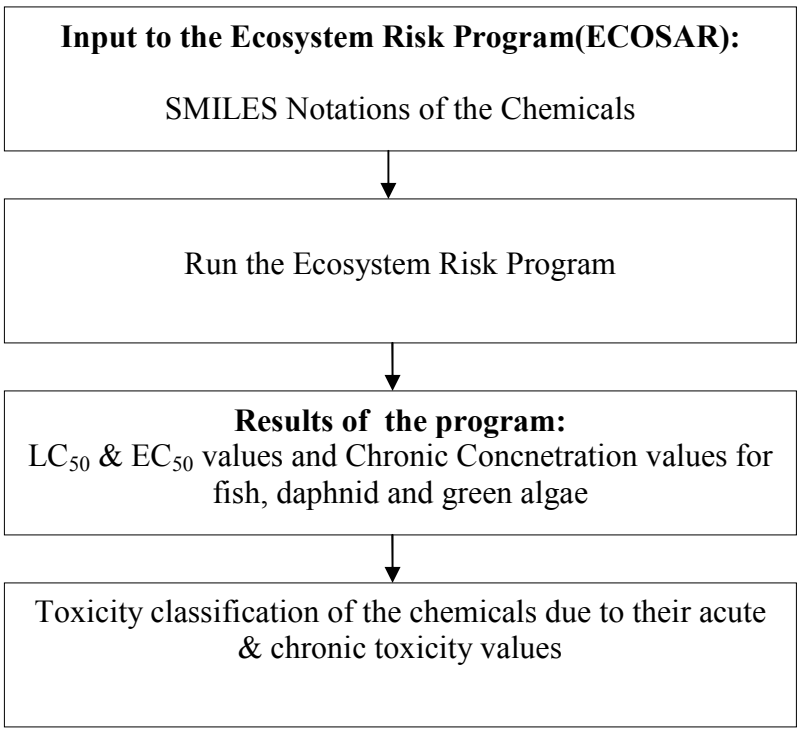

Figure 3.6 The Approach Used to Determine the Aquatic Toxicity of Chemicals

Table 3.5 ECOSAR Results for Glycerol

ECOSAR Class	Organism	Duration	End Point	Predicted concentration (ppm)
Neutral Organics	Fish	96-hr	LC_{50}	1.84×10^5
	Fish	14-day	LC_{50}	1.87×10^5
	Daphnid	48-hr	LC_{50}	1.53×10^5
	Green Algae	96-hr	EC_{50}	7.77×10^4
	Fish	30-day	ChV	1.32×10^4
	Daphnid	16-day	EC_{50}	1.59×10^3
	Green Algae	96-hr	ChV	9.43×10^2
	Fish (SW)	96-hr	LC_{50}	7.22×10^3

Table 3.6 Parameters for Acute & Chronic Toxicity Classification [30]

Organism	Acute Toxicity Value	Chronic Toxicity Value
Fish	96-hour LC_{50}	30-day ChV
Daphnid	48-hour LC_{50}	ChV or 16-day EC_{50}
Green algae	72 or 96-hour EC_{50}	ChV

Table 3.7 Acute and Chronic Toxicity Classification Criteria [30]

Environmental Concern	Selected ECOSAR Results
Low Toxicity	All three acute values are>100 mg/L AND all three chronic values are >10 mg/L
Moderate Toxicity	Any of the three acute values are>1.0 mg/L and <100mg/L, OR any of the chronic values are>0.1 mg/L and <10 mg/L
High Toxicity	Any of the three acute values are<1.0 mg/L, OR any of the chronic values are < 0.1 mg/L

3.4 Economical Criteria Selection and Use at the Conceptual Design Stage

The economical feasibility of processes at the conceptual design stage is significant for screening of alternative production pathways. The evaluation of the alternative processing routes is achieved considering the costs of raw materials, manufacturing costs and the product revenue. The economical potential of a processing route can be expressed as:

$$\Delta = \text{Product Revenue} - \text{Raw Material Costs} - \text{Manufacturing Costs} \qquad (3.4)$$

where, Δ is the economical potential with a unit of \$ / kg of product.

The economical potential of processes considered throughout the analysis needs to be modified since manufacturing costs for novel production routes are not available. For some of the production routes the product, by-product(s) and raw material prices can be obtained. Thus, Δ is replaced by Δ' indicating that manufacturing costs are not to be considered at this stage of process development since modified economical potential is used for screening purposes.

The second consideration in this part is related with the non-availability of the chemical prices to perform the analysis at any desired year. The price information is obtained from Chemical Marketing Reporter [32]. The cost and density of industrial gases and the density values are also obtained from the literature [33 &34]. After examining the technical grade market prices of the chemicals between the years 1997 – 2005, it is observed that the prices of the chemicals are nearly steady or show little fluctuations in 2002. Hence, the 2002 prices are utilized for most of the chemicals in the economical analysis. Although it is required to have latest price information for comparison of economical potential of the processing routes, chemical cost indexes are not available for each type of chemical. Also, the use of cost indexes for industrial chemicals will affect the market price of each chemical with same extent. Therefore, economical potential calculation with 2002 prices presents a relative comparison for the processing routes giving an indication about the feasibility of the routes.

3.5 Evaluation of Atom & Mass Efficiency at the Conceptual Design Stage

Atom efficiency is the ratio of the number of a specific atom present in the desired product to that in the reactants. **Mass efficiency** is the ratio of the mass converted to the desired product to the mass of reactants entering [13]. Therefore, the use of atom and mass efficiencies helps to determine the amount of wasted raw materials in a process. If the efficiency of the process is high, then the process favors more products and minor amount of the reactants are wasted.

In this study, first the atom and mass efficiencies of the biochemical routes are considered. The values are compared with the calculated atom and mass efficiencies of the petrochemical routes. For the atom and mass efficiency calculations, the reaction

equations for the production routes are used. A sample calculation about the atom & mass efficiencies of the processing routes is provided in Appendix C.

3.6 The Gibbs Free Energy of Major Reactions and the Economical Potential

The Gibbs free energy of reactions provides information about the spontaneity of the reactions. When $\Delta G<0$, the reaction is spontaneous. The spontaneity of the reactions might have an effect in reducing the cost of conversions and provide a measure for high economical potentials of processes. Therefore, it is reasonable to look for a correlation between the free energy change of major reactions and the economic potential of a process route. To seek for a correlation, petrochemicals for which price information and process information are available in the literature are selected [31]. The Gibbs free energy of reactions is calculated using the standard free energy of formation values for the raw materials and products by the following equation:

$$\Delta G^0_{rxn} = \Delta G^0_{PRODUCTS} - \Delta G^0_{REACTANTS} \qquad [35] \qquad \text{(at 25 ˚C \& 1 atm)} \qquad (3.5)$$

For chemicals for which Gibbs free energy of formation information data are unavailable, an estimation method developed by Joback based on the structure-activity relationships is used [36]. Details of the method are presented in Appendix D.

With the free energy of reactions calculated or estimated a plot of the modified economical potentials of processes versus the free energy of the major reactions of processes is prepared.

3.7 Environmental Performance Evaluation at the Preliminary Design Stage for 1,3 Propanediol Production

Up to this point, the criteria which are selected for screening of process alternatives at the conceptual design stage (stage 1) are examined. Next stage in the design of chemical processes is the preliminary design stage (stage 2). Because for most

chemicals considered in the conceptual design stage further data are not available, it is hard to perform the next step of analysis for most of the chemicals. During a search for potential processes via a biochemical route, the production of 1,3 propanediol from glycerol has been found to be attractive. Hence, this section describes the methodology which is selected and applied for the production of 1,3 propanediol from glycerol with biochemical production routes.

For stage 2, that is the preliminary design stage, it is possible to conduct an environmental performance analysis using detailed process data obtained either from laboratory or pilot plant studies. This process information can be used in material and energy balance calculations. Additionally, one can determine energy supply or removal from the processes using balances around the units in concern. This will further provide for calculation of electricity & fuel usage and water & steam consumption values. Use of fuels causes emissions of gases which should be taken into consideration during environmental assessment of the processes. The criteria that is selected and utilized at this stage are [13]:

- **Total mass of materials** used directly in the product, **minus the mass of the product**, per unit of manufactured output
- **Energy consumed** from electricity **converted to equivalent fuel use**, based on an average efficiency of converting energy to electricity
- **Water consumption** (contact cooling water) per unit of **manufactured output**
- **Emissions of CO & CO_2** per unit of manufactured output
- **Emissions of NO_x and SO_2** per unit of manufactured output

The evaluation of the second stage is performed utilizing material and energy balances for the 1,3 propanediol production routes. Here, it is significant to note that, the biochemical processing routes that are considered here include the conversion of glycerol to 1,3 propanediol with two different type of microorganisms, specifically *Klebsiella pneumoniae* and *Clostridium butyricum* strains. It is provided in the literature that *Klebsiella pneumoniae* is pathogenic, however the articles including its use in

laboratory-scale and pilot-scale 1,3 propanediol production do not mention the hazardous effects of the microorganism on humans.

In this stage, first it is important to specify design basis and assumptions related for the processes. Then, using reactions involved, block diagram representation of the processes are prepared. First common features for both biochemical processes will be provided. Then, differing features of the processes will be presented.

Table 3.8 Common Features of Design Basis and Assumptions for the Biochemical Production of 1,3 Propanediol

Plant capacity	10,000 tons 1,3 propanediol / year
Operation time	330 days / year (24 h operation)
Operation type	Continuous operation
Feed stream	Glycerol (70 wt %) & water (30 wt %)
Boiler type	Utility Boiler (Controlled- low NO_X burners)
Fuel type for boiler	Natural Gas
Heating Value for natural gas	37.23 kJ/m^3 [13]
Steam properties:	
Pressure	790 kPa [78]
Temperature	441.25 K (Saturation Temperature)
Cooling water properties:	
Inlet Temperature	288.15 K
Outlet Temperature	298.15 K

Table 3.8 (cont'd) Common Features of Design Basis and Assumptions for the Biochemical Production of 1,3 Propanediol

Process efficiencies:	
Boiler efficiency	0.75 - 0.90 [13] (0.80 is used)
Electric Motor	0.75 - 0.95 (0.85 is used)

The plant production capacity is considered as 10,000 tons of 1,3 propanediol /year. The reason is that the product cost estimation for a 10,000 tons/ year plant makes microbial process more attractive than the chemical route [14]. Here, it is important to note that the selection of this plant capacity has no effect on the environmental performance analysis, since the emissions of certain gases to the atmosphere, material & energy consumption and cooling water requirement values are found per kg of manufactured output.

The inlet feed stream is considered as industrial glycerol. Here, one approximation is made. Although industrial glycerol may include potassium and sodium salts, non-glycerol organic matters; the amount of these impurities is small when the amount is compared with the amount of water. Therefore, as a further simplification 70 wt% glycerol & 30 wt % water is assumed as the feedstock composition.

Operation time & type, utilized cooling water & steam properties, the type of the boiler are also common for both of the 1,3 propanediol production processes. Steam is considered to be used to remove water from the inlet and outlet feed streams by supplying the necessary heat of evaporation. The steam is selected as medium pressure steam and considered at its saturation temperature. The steam boiler works with natural gas combustion and it is selected as controlled to have low nitrous oxide emissions.

The electric motor is considered for pumping of cooling water in the plant. The motor efficiency value ranges from 0.75 to 0.95 and the electric motor efficiency is selected as 0.85. Also, here, the fuel type is not certain. Therefore, values for carbon dioxide, nitrogen oxides and sulfur dioxide emissions are approximated by using the

average values of coal-fired, petroleum-fired and gas-fired steam-electric generating units.

The differing features of the two microbial processes are shown in Tables 3.9 & 3.10.

Table 3.9 Design Basis and Features of 1,3 Propanediol Production Plant with *Klebsiealla pneumoniae* DSM 2026

Feedstock	Industrial glycerol (70 wt % glycerol & 30 wt% water)
Main products	1,3 propanediol, acetic acid, H_2,CO_2,H_2O
Microorganism type	Klebsiella pneumoniae DSM 2026
Operating conditions:	
Inlet temperature	298.15 K
Outlet temperature	310.15 K
Reaction temperature	310.15 K
Pressure	1 atm
Conversion	0.55 g 1,3 propanediol / g of glycerol
Separation scheme	Removal of water and acetic acid from the outlet stream

Table 3.10 Design Basis and Features of 1,3 Propanediol Production Plant with *Clostridium butyricum* F2b

Feedstock	Industrial glycerol (70 wt % glycerol & 30 wt% water)
Main products	1,3 propanediol, butyric acid,CO_2,H_2O
Microorganism type	Clostridium butyricum F2b

Table 3.10 (cont'd) Design Basis and Features of 1,3 Propanediol Production Plant with *Clostridium butyricum* F2b

Operating conditions:	
Inlet temperature	298.15 K
Outlet temperature	306.15 K
Reaction temperature	306.15 K
Pressure	1 atm
Conversion	0.55 g 1,3 PDO / g of glycerol
Separation scheme	Removal of water and butyric acid from the outlet stream

For both processes specification for inlet glycerol is 70 wt% glycerol. The remaining portion is water. For the conversion of glycerol to 1,3 propanediol an approximate reaction stoichiometry is assumed by Deckwer [38]. Glycerol is assumed to be completely consumed further assuming that only acetic acid is obtained as the main by-product. Similarly, for the second plant, reaction stoichiometry is constructed for *Clostridium butyricum* and the main by-product is taken as butyric acid. Details of the mechanisms for glycerol metabolism are provided in Appendix E.

Taking into consideration the process data and the reaction stoichiometry, and yields, material & energy balance calculations are performed and the second stage metrics are calculated. For energy balance calculations, the approach adopted is summarized in Figure 3.7.

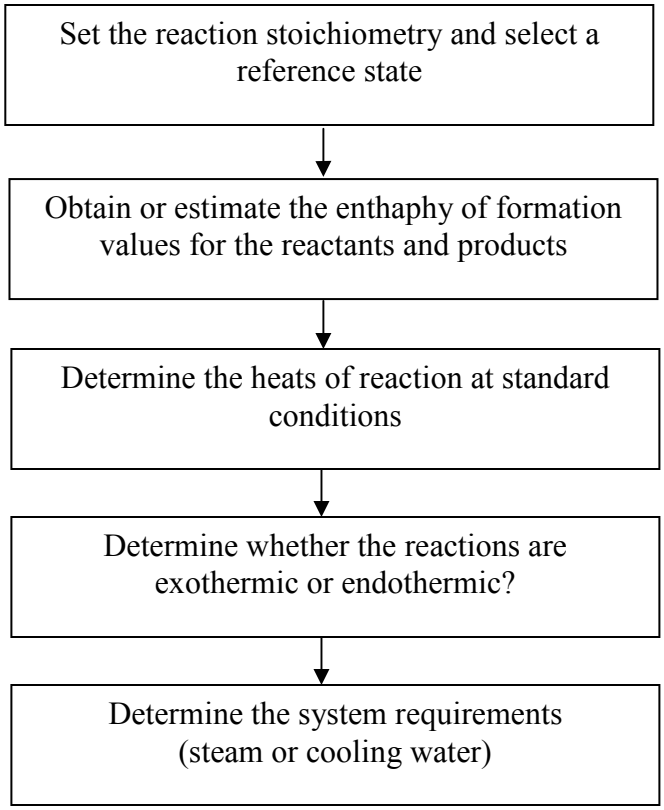

Figure 3.7 Determination of the Heats of Reaction and the System Requirements

First, it is required to select a reference state and obtain the enthalpy of formation values for the inlet and outlet stream components. If the enthalpy of formation value for a chemical is available, then this value is used in the analysis. If the value is not accessible, then a group contribution method (Joback method [36], Appendix D) to estimate the enthalpy of formation values from structures of the chemicals is used. Afterwards, process requirements such as steam for heating purposes or cooling water for heat removal are determined.

As it is indicated in Figure 3.8, the results of material and energy balances can be utilized to obtain the second stage metrics. Material balance provides the calculation of material consumption per kg of manufactured product and the CO_2 emissions to the atmosphere resulting from the reaction. Energy balance provides to have information on

the amount of cooling water and steam usage in the heat exchange equipment. This is considered utilizing the energy balance equation provided in the below equation.

$$\Delta \dot{H} + \Delta \dot{E}_K + \Delta \dot{E}_p - \dot{Q} + \dot{W}_s = 0 \tag{3.6}$$

In the use of Equation 3.6, kinetic, potential energy terms and shaft-work required for mixing operation are neglected. Heat capacity of cooling water is taken as 4.1815 kJ/kg. K and the temperature difference for cooling water is taken as 10 K.

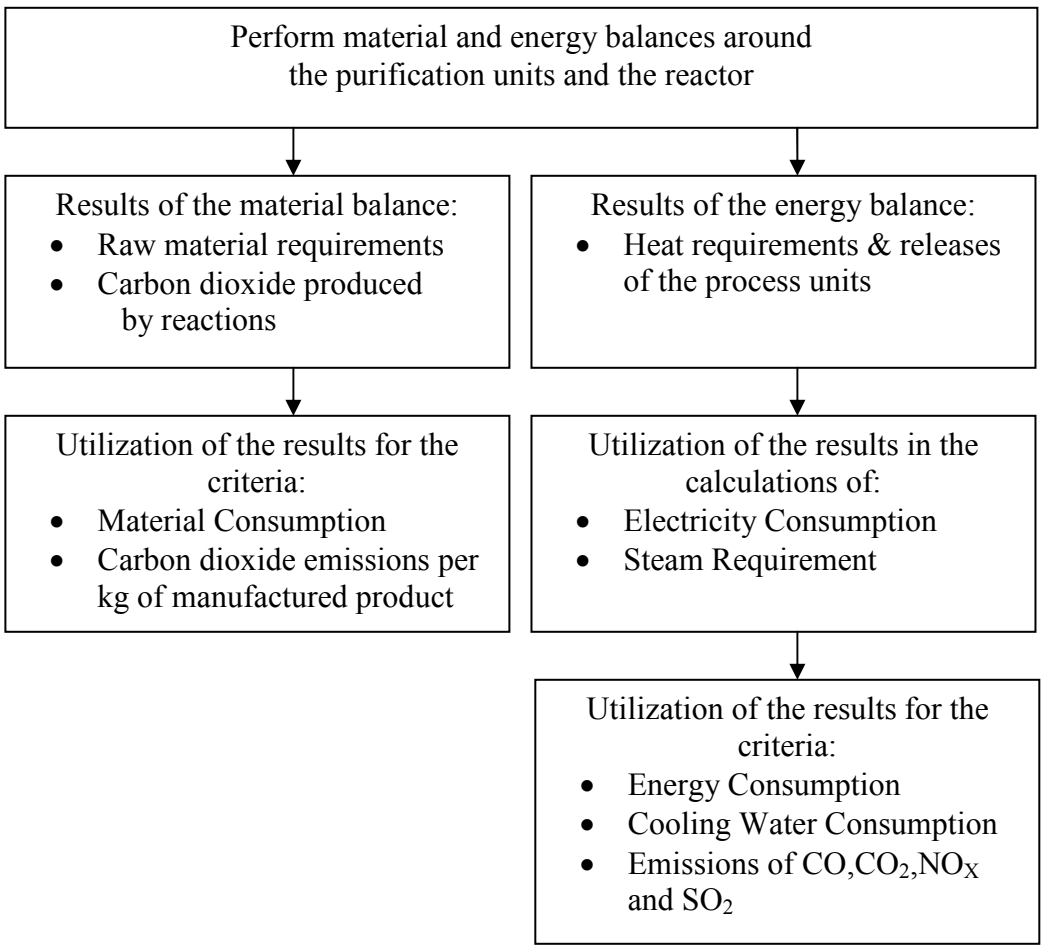

Figure 3.8 The Approach Used to Evaluate Environmental Performance Metrics at Stage 2

After the calculation of cooling water and steam requirements, it is needed to estimate the emission of gases due to natural gas combustion for steam and cooling water use. The emission due to natural gas combustion can be calculated with the following equation [13]:

$$E\ (kg/\ unit\ /yr): (ED) \times (FV)^{-1} \times (EF) \times (BE)^{-1} \quad (3.7)$$

where;

ED: Energy demand of the unit per year (energy demand/unit/year)

FV: Fuel value (energy/volume of fuel combusted)

EF: Emission factor from fossil-fuel steam-electric generating units (kg/volume of fuel combusted)

BE: The boiler efficiency (range from: 0.75 - 0.90, is used as 0.80)

The boiler efficiency and the fuel value are given in Table 3.8. Energy demand term is calculated by the energy balance. The only unknown in Equation 3.7 is emission factor. Emission factors for sulfur dioxide (SO_2), nitrogen oxides (NO_X), carbon monoxide (CO) and carbon dioxide (CO_2) are given in Table 3.11 [13].

Table 3.11 Emission Factors for SO_2, NO_X, CO and CO_2 for Natural Gas Combustion

Combustor Type	SO_2 kg/10^6 m^3	NO_X kg/10^6 m^3	CO kg/10^6 m^3	CO_2 kg/10^6 m^3
Utility Boiler	9.6	2240	1344	1.9×10^6

Emission factors are used with Equation 3.7 to calculate the emission of combustion gases to atmosphere for the evaluation of the second stage metrics.

Possible emissions to atmosphere due to cooling water use are not reported in the literature. It is considered in this study that cooling water is circulated in the plant and it

is required to pump cooling water. Hence, cooling water cost is mainly due to cost of electricity consumption for pumping. Therefore, cooling water use could be linked to emissions due to electricity consumption for pumping. Using the cost of electricity per kWh, the electricity demand is calculated. The cost of utilities is presented in Table 3.12. Using the ranges given in Table 3.12, cost for steam is taken as $6/ 1000 kg of steam, the cost of cooling water as $0.045/ 1000 kg of cooling water and electricity is $0.05/ kWh.

Table 3.12 The Cost of Utilities in 2002 Used in the Analysis [37]

Type of Utility	Cost of Utility
Medium Pressure Steam (790 kPa)	$ 4.40-7.50 / 1000 kg of steam
Cooling water (Tower)	$ 0.02-0.07 / 1000 kg of cooling water
Electricity (Self-generated)	$ 0.030-0.075 / kW.h

Emissions of CO_2, NO_X and SO_2 are calculated using equation 3.8 [13]:

$$E \text{ (kg/ unit /yr)}: (ED) \times (EF) \times (ME)^{-1} \quad (3.8)$$

where;

ED: Electricity demand of the unit per year (electricity demand/unit/year)

EF: Emission factor from fossil-fueled steam-electric generating units

ME: The efficiency of the electric motor (range from: 0.75 - 0.95)

It is suggested that if the fuel type is not known, emission of CO_2, SO_2 and NO_X to the atmosphere can be averaged using the total values for fossil-fuel steam generators [13]. Emission factors for various fuels can be indirectly calculated from data reported in Table 3.13. These are reported in Table 3.14.

Table 3.13 Emission of CO_2, SO_2 and NO_X to Atmosphere in Power Plants [13]

Emission (thousands of short tons)	Coal Fired	Petroleum Fired	Gas Fired	Total
CO_2	14.99×10^5	87.7×10^3	1.56×10^5	1.75×10^6
SO_2	14×10^3	6.37×10^2	1	1.48×10^4
NO_X	6.9×10^3	2.08×10^2	5.99×10^2	7.69×10^3
Power generated (billion kW.h)	1.55×10^3	1.11×10^2	2.64×10^2	2.79×10^3

* 1 short ton equals to 0.8929 metric tons

Table 3.14 Average Values of the Emission Factors for CO_2, NO_X, SO_2

Chemical Name	Emission Factor (kg /kWh)
CO_2	0.56×10^{-7}
NO_X	4.74×10^{-9}
SO_2	2.46×10^{-9}

Sample calculations for both production routes are provided in Appendix F.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Persistence Classification of Chemicals

Persistence of chemicals is considered in air and water. Initially, persistence in air is examined. Persistence classification in air is determined by the rate constants for atmospheric oxidation reactions of organic chemicals with hydroxyl radicals and ozone and atmospheric half-life values of the chemicals. Rate constants and degradation half-life values for bio-based building blocks are given in Table 4.1.

Table 4.1 Rate Constants for Atmospheric Oxidation Reactions of Bio-based Building Blocks with Hydroxyl Radicals & Ozone and Overall Degradation Half-lives

Bio-based Building Blocks	Hydroxyl radicals rate constant (cm^3/ molecule.s)	Hydroxyl radicals half-life (days)	Ozone rate constant (cm^3/ molecule.s)	Ozone half-life (days)	Overall half-life (days)
Glycerol	18.73 E-12	0.571	Not Estimated	NE	0.571
3-HPA	5.54 E-12	1.93	NE	NE	1.93
Levulinic Acid	4.22 E-12	2.54	NE	NE	2.54
Sorbitol	49.97 E-12	0.21	NE	NE	0.21
Succinic Acid	2.76 E-12	3.87	NE	NE	3.87
2,5 FDCA	5.13 E-12	2.09	NE	NE	2.09

Table 4.1 (cont'd) Rate Constants for Atmospheric Oxidation Reactions of Bio-based Building Blocks with Hydroxyl Radicals & Ozone and Overall Degradation Half-lives

Bio-based Building Blocks	Hydroxyl radicals rate constant (cm^3/ molecule.s)	Hydroxyl radicals half-life (days)	Ozone rate constant (cm^3/ molecule.s)	Ozone half-life (days)	Overall half-life (days)
Glutamic Acid	40.96 E-12	0.26	NE	NE	0.26
Glucaric Acid	34.67 E-12	0.31	NE	NE	0.31
Aspartic Acid	39.54 E-12	0.27	NE	NE	0.27
Itaconic Acid	19.73 E-12	0.54	1.14 E-17	1.0	0.35
3-Hydroxy-butyrolactone	8.19 E-12	1.32	NE	NE	1.32
Xylitol	39.56 E-12	0.27	NE	NE	0.27

In Table 4.1, 'NE' means that EPISuite does not estimate the rate constant with ozone, since no structural match is obtained. Considering the persistence criteria described in the methodology section, levulinic acid, succinic acid and 2,5 furandicarboxylic acid (2,5 FDCA) are classified as highly persistent chemicals as they have a half-life value greater than 2 days.

The persistence of bio-based building blocks in water is determined by the use of biodegradation half-life values in water. As can be seen in Table 4.2, biodegradation half-life values for bio-based building blocks in water changes from 2.3 to 15 days. Since these values are less than 2 months, bio-based building blocks are classified as being not persistent in water.

Table 4.2 The Biodegradation Index and Half-life Values for Bio-based Building Blocks in Water

Bio-based Building Blocks	Biodegradation Index	Biodegradation Half-life in water (days)
Glycerol	3.4756	8.7
3 HPA	3.5247	8.7
Levulinic Acid	3.2847	15
Sorbitol	3.7564	8.7
Succinic Acid	3.6674	8.7
2,5 FDCA	3.0300	15
Glutamic Acid	3.6277	8.7
Glucaric Acid	4.1039	2.3
Aspartic Acid	3.6587	8.7
Itaconic Acid	3.6409	8.7
3-Hydroxybutyrolactone	3.2737	15
Xylitol	3.6628	8.7

Distribution of the bio-based building blocks in different compartments when they are released to the environment is determined by the results of Level-III fugacity model. PBT Profiler results are presented in Figure 4.1 & 4.2. The bio-based building blocks will be mainly in soil and water if any release of these raw materials takes place.

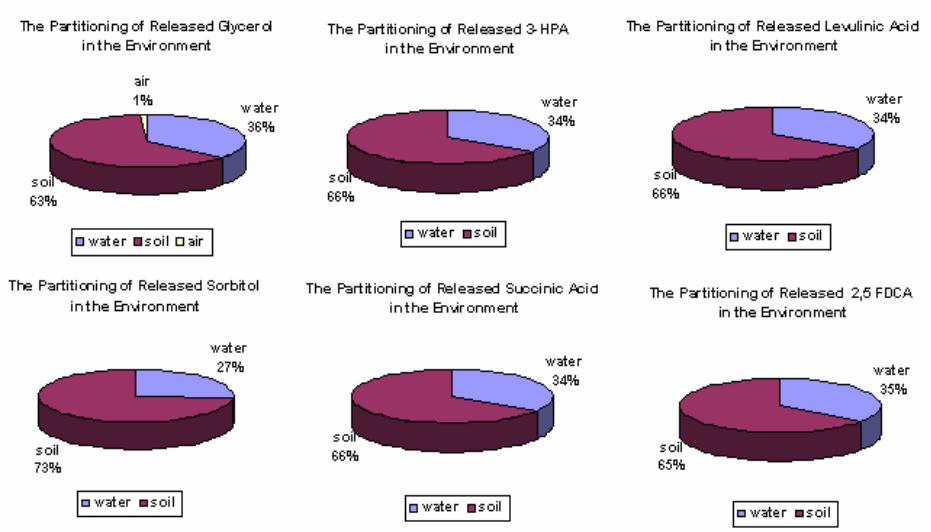

Figure 4.1 Distribution of Glycerol, 3-HPA, Levulinic, Succinic Acids, Sorbitol, 2,5 FDCA in Environmental Compartments In Case of a Release to the Environment

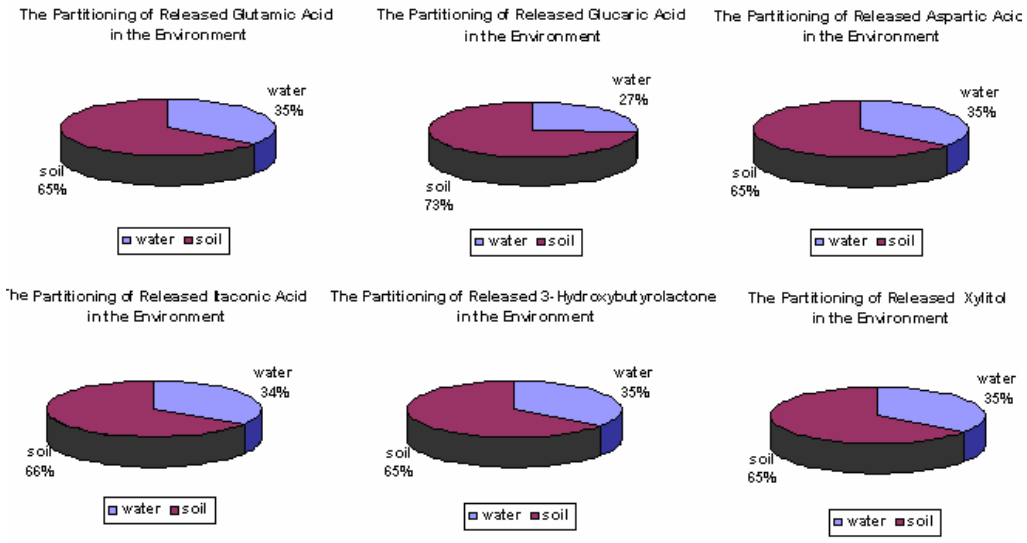

Figure 4.2 Distribution of Glutamic, Glucaric, Aspartic, Itaconic Acids, 3-Hydroxybutyrolactone, Xylitol in Environmental Compartments In Case of a Release to the Environment

Persistence classification of petroleum-based raw materials is achieved with the degradation half-life values in air and water as reported in Table 4.3. Persistence of acetic acid, acetylene, acrylonitrile, citric acid, cyanoacetic acid, dihydroxyacetone, epichlorohydrin, ethylene cyanohydrin, ethylene oxide, gamma-butyrolactone, lactic acid, maleic anhydride, potassium cyanide, succinic anhydride and trimethylene cyanide in air is high. Persistence of the raw materials in water is classified as low.

Table 4.3 Degradation and Biodegradation Half-life Values of Petroleum-based Raw Materials in Air and Water Compartments of the Environment

Petroleum-based Building Blocks	Degradation & Biodegradation Half-life (days)	
	Air	Water
Acetic Acid	22	8.7
Acetylene	18	15
Acrolein	0.79	15
Acrylic Acid	1.3	8.7
Acrylonitrile	3.8	15
Allyl Alcohol	0.96	15
1, 3 butadiene	0.2	15
Butane 1,2,4 triol	0.79	8.7
Citric Acid	2.3	8.7
Cyanoacetic Acid	25	8.7
Dihydroxyacetone	3.1	8.7
Epichlorohydrin	620	15
Ethylene	1.5	15
Ethylene Cyanohydrin	21	15

Table 4.3 (cont'd) Degraration and Biodegradation Half-life Values for Petroleum-based Raw Materials in Air and Water Compartments of the Environment

Petroleum-based Building Blocks	Degradation & Biodegradation Half-life (days)	
	Air	Water
Ethylene oxide	210	15
Formaldehyde	1.7	15
Gamma-butyric Acid	0.46	8.7
Gamma butyrolactone	7.1	15
Ketene	0.92	15
Lactic Acid	2.7	8.7
Maleic Anhydride	4.1	15
Methyl Amine	0.71	15
Potassium Cyanide	180	15
Propylene	0.38	15
Succinic Anhydride	35	15
Tetrahydrofuran	1	15
Tetrahydrofurfuryl Alcohol	0.67	15
Trimethylene Cyanide	36	15

Distribution of the petrochemical feedstocks in the environmental compartments when they are released to the environment is presented in Figures 4.3-4.7. It is concluded that the petrochemical building blocks mostly tend to be in water and soil compartments similar to the biochemical ones. Within the highly persistent group, acetic acid, acetylene, acrylonitrile, dihydroxyacetone, epichlorohydrin, ethylene oxide, gamma-butyrolactone, lactic acid, maleic anhydride, succinic anhydride and

trimethylene cyanide show some presence in air if a release occurs. The rest of highly persistent petrochemicals in air do not show a presence in air if a release occurs.

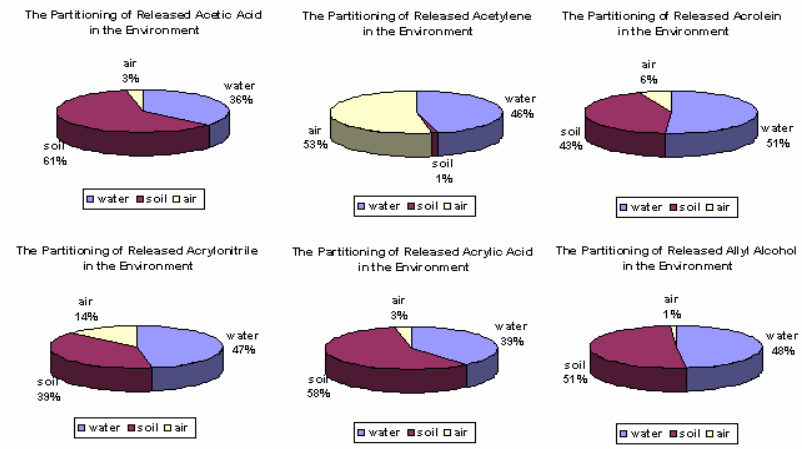

Figure 4.3 Distribution of Acetic Acid, Acetylene, Acrolein, Acrylonitrile, Acrylic Acid and Allyl Alcohol in Environmental Compartments In Case of a Release to the Environment

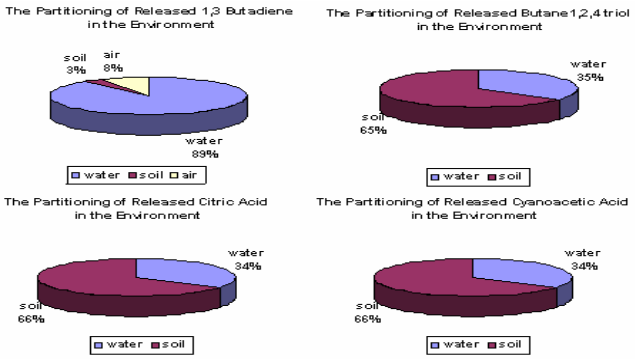

Figure 4.4 Distribution of 1,3 Butadiene, Butane 1,2,4 triol, Citric Acid and Cyanoacetic Acid in Environmental Compartments In Case of a Release to the Environment

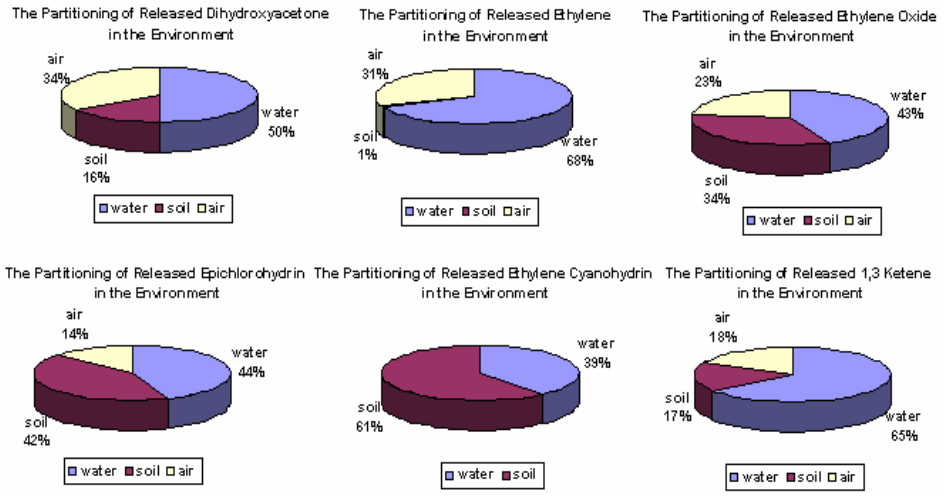

Figure 4.5 Distribution of Dihydroxyacetone, Ethylene, Ethylene Oxide, Epichlorohydrin, Ethylene Cyanohydrin and Ketene in Environmental Compartments In Case of a Release to the Environment

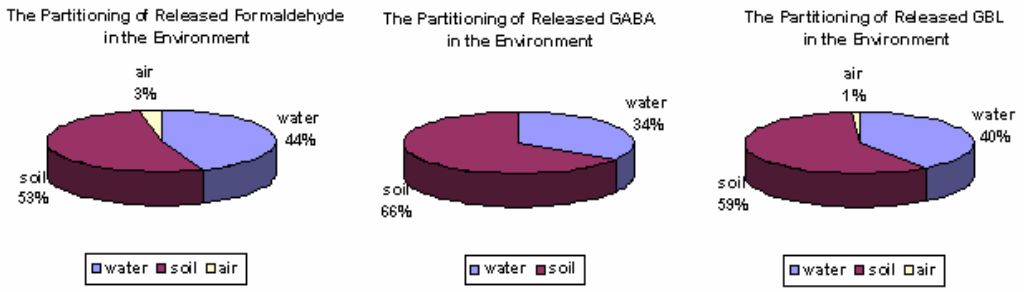

Figure 4.6 Distribution of Formaldehyde, Gamma-butyric acid (GABA) and Gamma-Butyrolactone (GBL) in Environmental Compartments In Case of a Release to the Environment

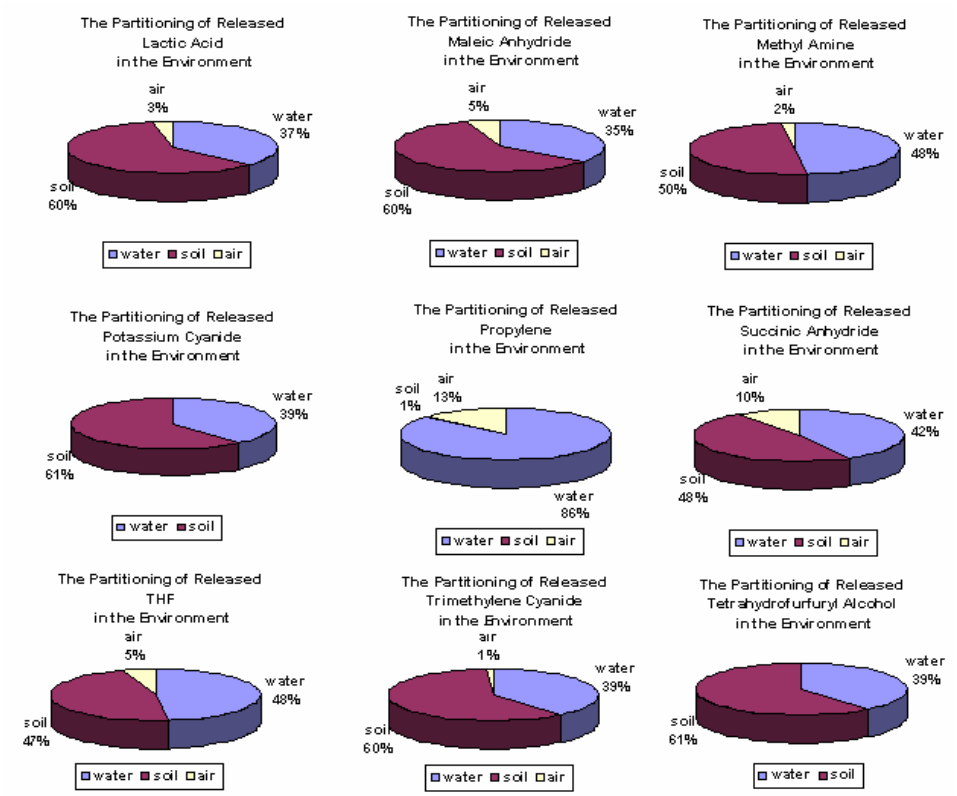

Figure 4.7 Distribution of Lactic Acid, Maleic Anhydride, Methyl Amine Potassium Cyanide, Propylene, Succinic Anhydride, Tetrahydrofuran, Trimethylene Cyanide and Tetrahydrofurfuryl Alcohol in Environmental Compartments In Case of a Release to the Environment

Degradation and biodegradation half-life values for bio-based building block derivatives are presented in Tables G.1-12 in Appendix G.

Degradation half-life values in air for propanol, glycidol, acrylonitrile, ethyl-3HP, malonic acid, propiolactone, glucarodilactone, 3-4 methyl GBL, glutaric acid, g-valerolactone, ethylene glycol, lactic acid, DBE, GBL, succinonitrile, succinic acid and epoxy lactone exceed the persistence criteria in air and these chemicals are classified as 'highly persistent in air'. None of the derivatives is persistent in water.

The distribution of the derivatives in the environmental compartments in case of a release is given in the following figures.

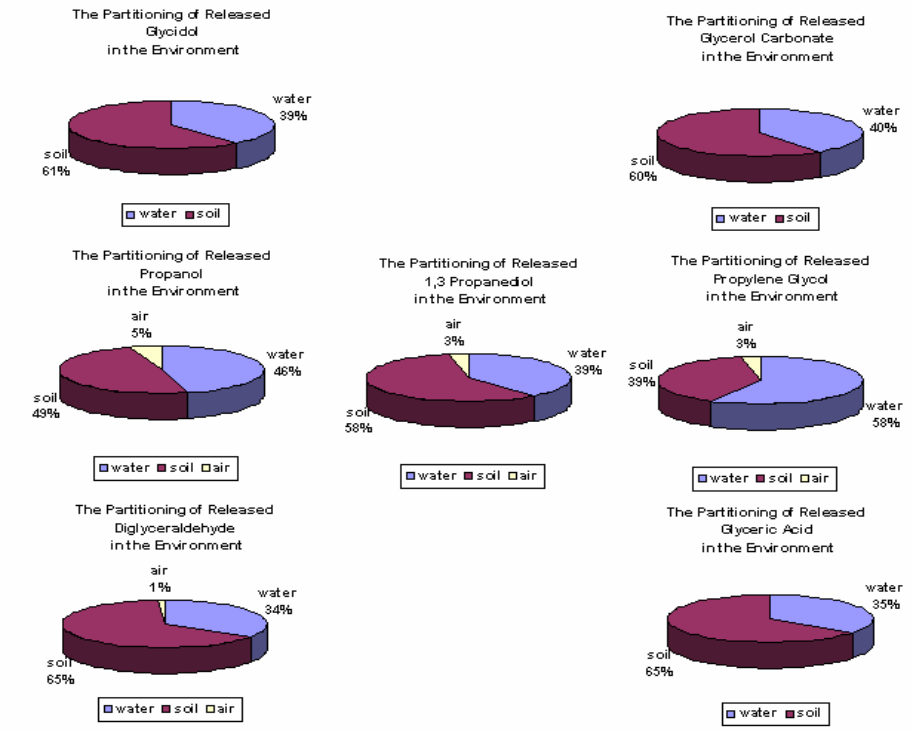

Figure 4.8 Distribution of Glycerol Derivatives In Environmental Compartments In Case of a Release to the Environment

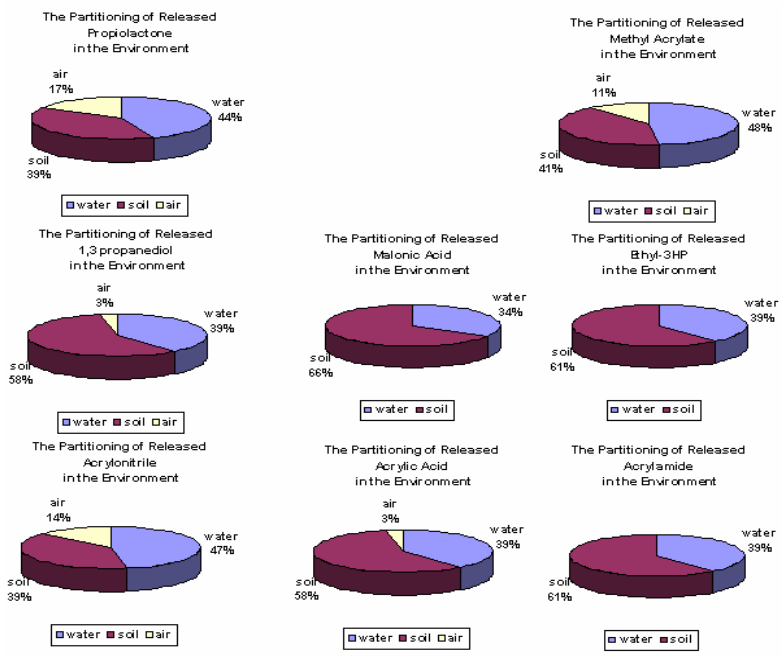

Figure 4.9 Distribution of 3-HPA Derivatives In Environmental Compartments In Case of a Release to the Environment

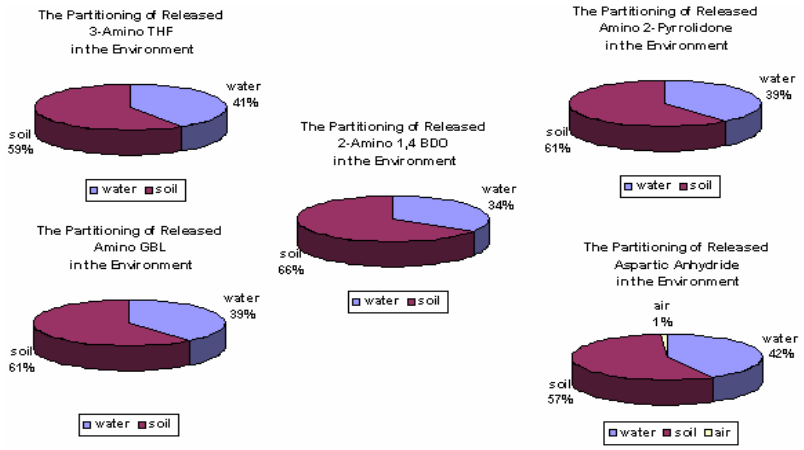

Figure 4.10 Distribution of Aspartic Acid Derivatives In Environmental Compartments In Case of a Release to the Environment

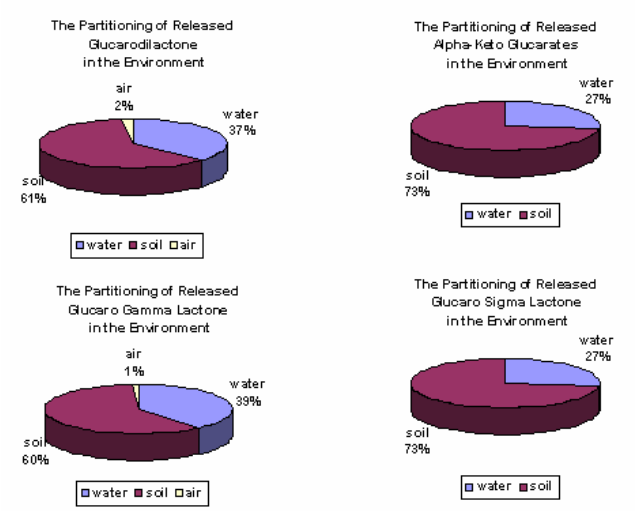

Figure 4.11 Distribution of Glucaric Acid Derivatives In Environmental Compartments In Case of a Release to the Environment

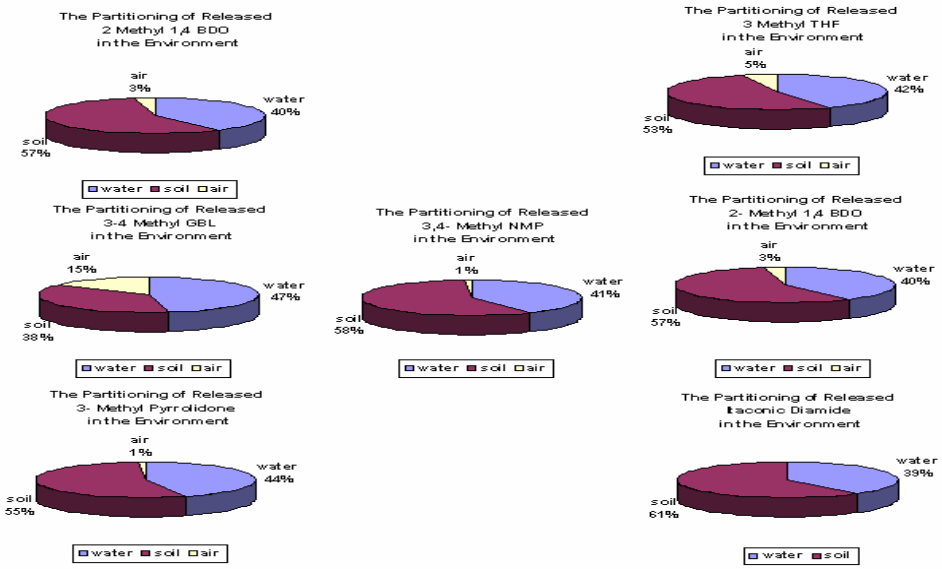

Figure 4.12 Distribution of Itaconic Acid Derivatives in Environmental Compartments In Case of a Release to the Environment

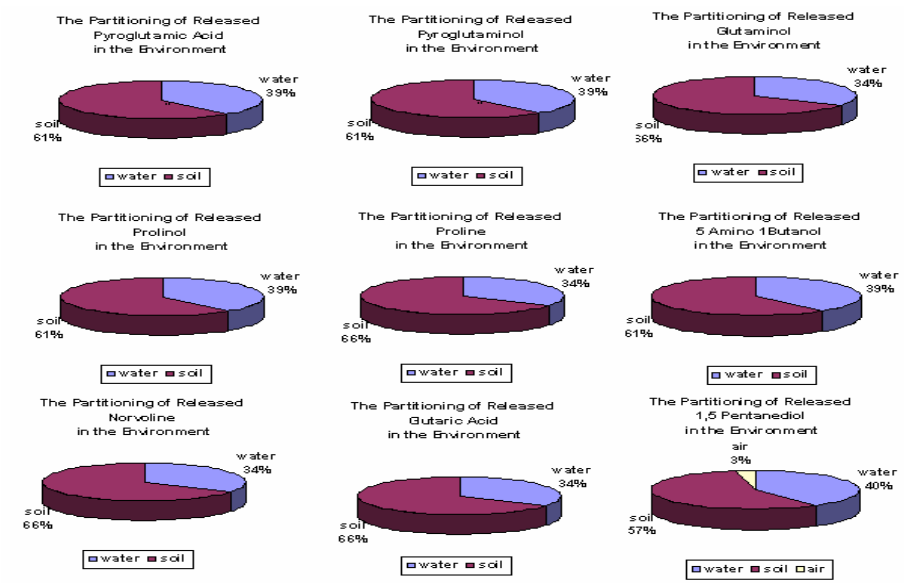

Figure 4.13 Distribution of Glutamic Acid Derivatives in Environmental Compartments In Case of a Release to the Environment

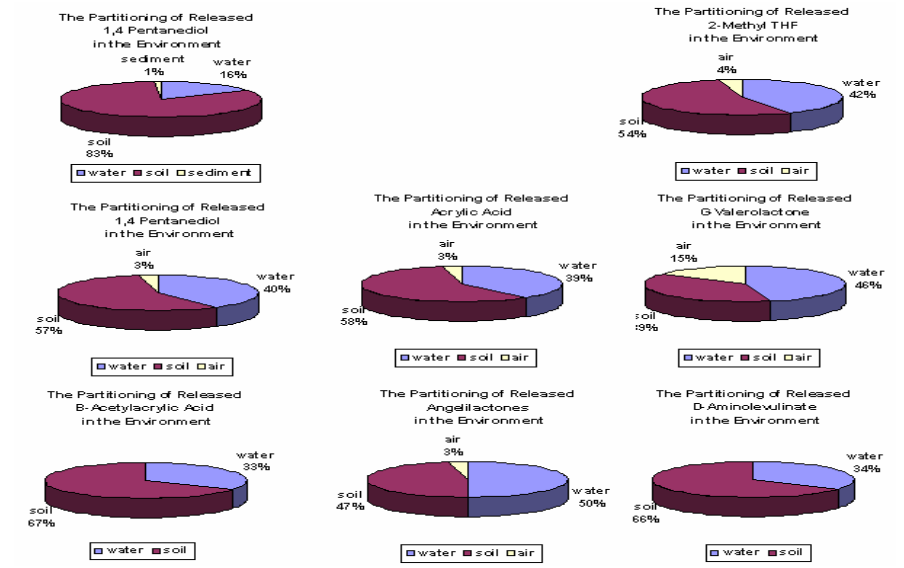

Figure 4.14 Distribution of Levulinic Acid Derivatives in Environmental Compartments In Case of a Release to the Environment

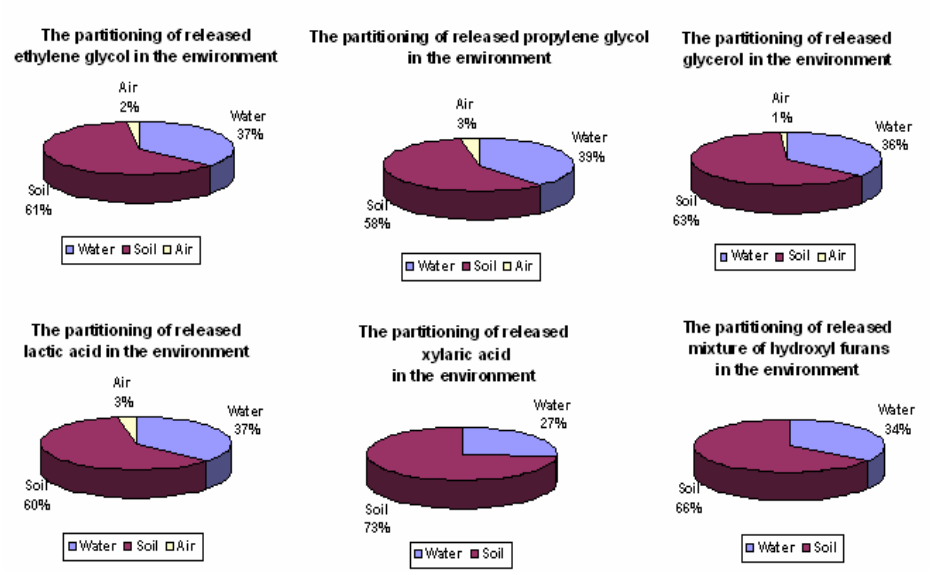

Figure 4.15 Distribution of Xylitol Derivatives in Environmental Compartments In Case of a Release to the Environment

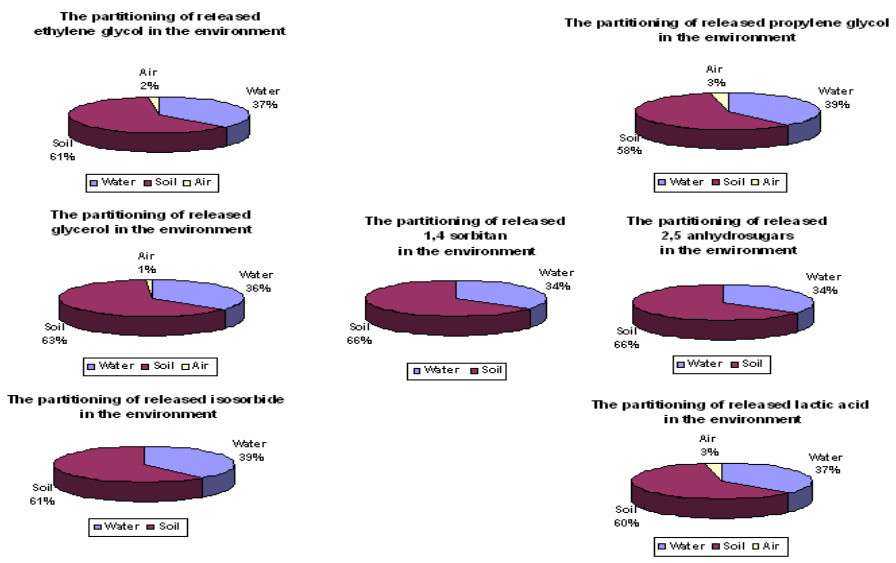

Figure 4.16 Distribution of Sorbitol Derivatives in Environmental Compartments In Case of a Release to the Environment

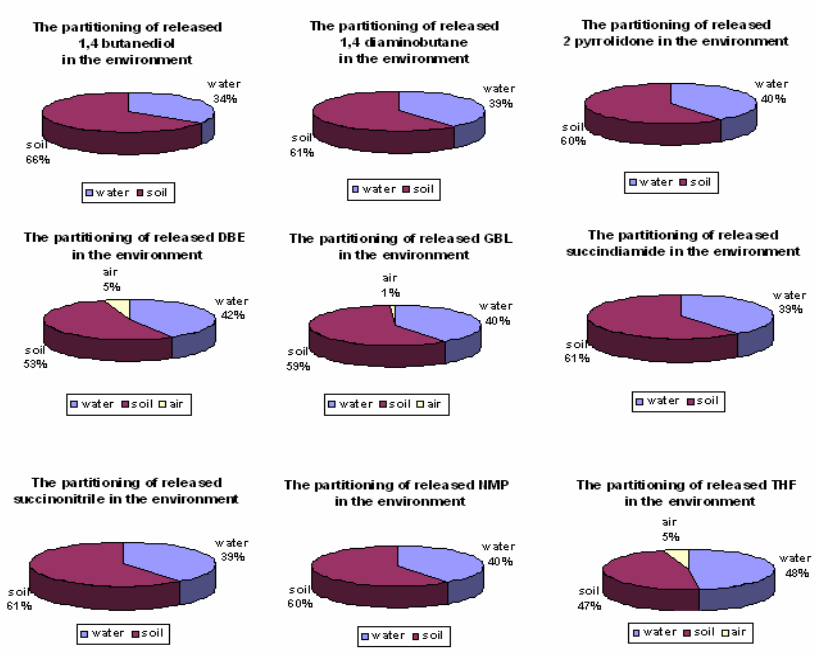

Figure 4.17 Distribution of Succinic Acid Derivatives in Environmental Compartments In Case of a Release to the Environment

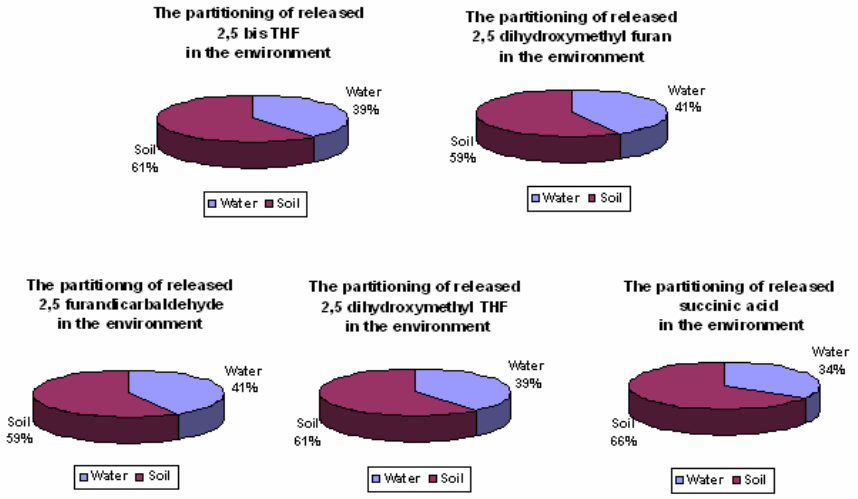

Figure 4.18 Distribution of 2,5 FDCA Derivatives in Environmental Compartments In Case of a Release to the Environment

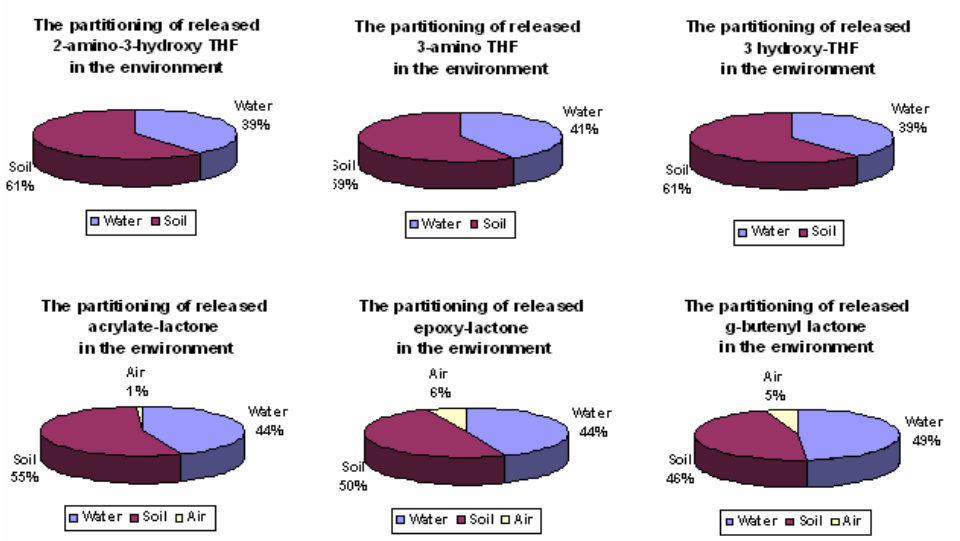

Figure 4.19 Distribution of 3-Hydroxybutyrolactone Derivatives in Environmental Compartments In Case of a Release to the Environment

When, in case of a release, the partitioning of the bio-based building block derivatives in the environment is examined; it is observed that chemicals are mostly present in water or soil. Of the highly persistent group of chemicals in air, propanol, acrylonitrile, propiolactone, glucarodilactone, 3-&4- methyl GBL, g-valerolactone, ethylene glycol and lactic acid, dibutyl ether (DBE), gamma-butyrolactone (GBL) and epoxy-lactone show some presence in air.

4.2 Bioaccumulation Classification of Chemicals

Bioaccumulation potential of the chemicals are determined by the use of bioconcentration factor (BCF) or the logarithmic value of the octanol-water partition coefficient (log K_{OW}). In Table 4.4, the values of BCF, log K_{OW} and bioaccumulation classification for bio-based building blocks are given.

Table 4.4 Bioconcentration Factor, Octanol-Water Partition Coefficient Values and Bioaccumulation Classification of Bio-Based Building Blocks

Bio-based Building Blocks	**Bioconcentration Factor**	**Log K_{OW}**	**Potential for bioaccumulation**
Glycerol	3.162	-1.6524	Low Potential
3-HPA	3.162	-0.8869	Low Potential
Levulinic acid	3.162	-0.4896	Low Potential
Sorbitol	3.162	-3.0108	Low Potential
Succinic acid	3.162	-0.7543	Low Potential
2,5 FDCA	3.162	0.8778	Low Potential
Glutamic acid	3.162	-3.8315	Low Potential
Glucaric acid	3.162	-2.5073	Low Potential
Aspartic acid	3.162	-4.3226	Low Potential
Itaconic acid	3.162	-0.3434	Low Potential
3-Hydroxybutyrolactone	3.162	-1.8442	Low Potential
Xylitol	3.162	-2.5580	Low Potential

Since all bioconcentration factors are less than 250 and the logarithmic value of the octanol-water partition coefficient is smaller than 3.5, bioaccumulation potential of all building blocks are classified as low. The reason why bioconcentration factors for all the building blocks are 3.162 is clarified with the description of BCFWIN in Appendix B.2. Similarly, when the bioconcentration values for the petroleum-based building blocks are estimated by the EPISuite, bioconcentration factor values for most of the chemicals are found as 3.162. The ones with values different from 3.162 are presented in Table 4.5.

Table 4.5 Bioconcentration Factor, Octanol-Water Partition Coefficient Values and Bioaccumulation Classification of Petrochemical Raw Materials with BCF Values Different from 3.162

Petroleum-based Building Block	Bioconcentration Factor	Log K_{OW}	Potential for bioaccumulation
1, 3 Butadiene	6.797	2.0330	Low Potential
Maleic anhydride	3.519	1.6187	Low Potential
Propylene	4.602	1.6783	Low Potential

In a similar manner, bioconcentration factors for most of the products are estimated by EPISuite as 3.162. The products having BCF values different from 3.162 are given in Table 4.6.

Table 4.6 Bioconcentration Factor, Octanol-Water Partition Coefficient Values and Bioaccumulation Classification of Products with BCF Values Different from 3.162

Derivative	Bioconcentration Factor	Log K_{OW}	Potential for bioaccumulation
3- methyl THF	2.202	1.3544	Low Potential
3- methyl pyrolidone	1.44	1.1148	Low Potential
2- methyl THF	2.202	1.3544	Low Potential

Bioaccumulation analysis shows that bioaccumulation potentials of all chemicals considered in this study are low.

4.3 Toxicity Classification of Chemicals

Toxicity of the chemicals is estimated utilizing acute and chronic concentration values of the chemicals for fish, daphnid and green algae obtained by ECOSAR and classifying these values to assess environmental concerns. The concentration values and toxicity classification for bio-based building blocks are reported in Table 4.7 & 8.

Table 4.7 Acute and Chronic Toxicity Concentration Values of Bio-Based Building Blocks for Fish, Daphnid and Green Algae

Bio-Based Feedstocks	ECOSAR Results					
	Organism					
	Fish		Daphnid		Green Algae	
	96-hour LC_{50} (ppm)	30-day ChV (ppm)	48-hour LC_{50} (ppm)	16-day EC_{50} (ppm)	96-hour EC_{50} (ppm)	96-hour ChV (ppm)
Glycerol	$1.84x10^5$	$1.32x10^4$	$1.53x10^5$	$1.59x10^3$	$7.77x10^4$	$9.43x10^2$
3-HPA	$3.48x10^5$	$2.81x10^4$	$3.05x10^5$	$4.42x10^3$	$1.62x10^5$	$3.04x10^3$
Aspartic Acid	$4.06x10^6$	-	$1.33x10^5$	-	$2.83x10^4$	$1.47x10^3$
Glucaric Acid	$2.70x10^7$	$1.68x10^6$	$2.12x10^7$	$1.51x10^5$	$1.02x10^7$	$7.55x10^4$
Itaconic Acid	$1.53x10^5$	$1.35x10^4$	$1.39x10^5$	$2.56x10^3$	$7.61x10^4$	$1.97x10^3$
Glutamic Acid	$2.18x10^6$	-	$7.59x10^4$	-	$1.91x10^4$	$1.12x10^3$
Levulinic Acid	$1.89x10^5$	$1.63x10^4$	$1.7x10^5$	$2.94x10^3$	$9.22x10^4$	$2.19x10^3$

Table 4.7 (cont'd) Acute and Chronic Toxicity Concentration Values of Bio-Based Building Blocks for Fish, Daphnid and Green Algae

Bio-Based Feedstocks	ECOSAR Results					
	Organism					
	Fish		Daphnid		Green Algae	
	96-hour LC_{50} (ppm)	30-day ChV (ppm)	48-hour LC_{50} (ppm)	16-day EC_{50} (ppm)	96-hour EC_{50} (ppm)	96-hour ChV (ppm)
Xylitol	$2.18x10^6$	$1.35x10^5$	$1.71x10^6$	$1.19x10^4$	$8.20x10^5$	$5.88x10^3$
Sorbitol	$6.92x10^6$	$3.97x10^5$	$5.24x10^6$	$3.00x10^4$	$2.46x10^6$	$1.36x10^4$
Succinic acid	$3.37x10^5$	$2.78x10^4$	$2.98x10^5$	$4.59x10^3$	$1.59x10^5$	$3.25x10^3$
2,5 FDCA	$1.31x10^4$	$1.41x10^3$	$1.30x10^4$	$4.07x10^2$	$7.60x10^3$	$3.98x10^2$
3 – Hydroxy butyrolactone	$1.75x10^3$	$8.98x10^3$	$2.53x10^5$	-	$1.21x10^2$	86.57

The acute and chronic toxicity values presented in Table 4.7 mean that if the building blocks reach the indicated concentrations in aqueous medium, these chemicals will be toxic to aqueous organisms. Taking into consideration the limit values for toxicity classification, since all values are in the range of low toxicity concern, all the bio-based building blocks are classified as having low toxicity potential.

Acute and chronic concentration values of petrochemical raw materials in aqueous media are presented in Table 4.8.

Table 4.8 Acute and Chronic Toxicity Concentration Values of Petroleum-Based Building Blocks for Fish, Daphnid and Green Algae

Petroleum-Based Feedstocks	ECOSAR Results					
	Organism					
	Fish		Daphnid		Green Algae	
	96-hour LC_{50} (ppm)	30-day ChV (ppm)	48-hour LC_{50} (ppm)	16-day EC_{50} (ppm)	96-hour EC_{50} (ppm)	96-hour ChV (ppm)
Acetic acid	$2.78x10^4$	$2.63x10^3$	$2.61x10^4$	$5.80x10^2$	$1.46x10^4$	$4.85x10^2$
Acetylene	$4.96x10^2$	50.19	$4.79x10^2$	12.75	$2.75x10^2$	11.55
Acrolein	17.39	6.45	37.53	-	$1.11x10^3$	39.11
Acrylonitrile	0.414	-	-	-	-	-
Allyl alcohol	0.304	0.029	-	-	-	-
Ammonia	$5.82x10^2$	56.38	$5.52x10^2$	13.05	$3.12x10^2$	11.21
1, 3 Butadiene	37.58	4.86	40.35	2.097	25.27	2.097
Butane 1,2,4 triol	$2.69x10^5$	$1.89x10^4$	$2.23x10^5$	$2.20x10^3$	$1.12x10^5$	$1.28x10^3$
Citric acid	$4.01x10^6$	$2.86x10^5$	$3.34x10^6$	$3.44x10^4$	$1.69x10^6$	$2.02x10^4$
Cyanoacetic acid	$2.48x10^5$	$2.05x10^4$	$2.19x10^5$	$3.36x10^3$	$1.17x10^5$	$2.37x10^3$
Dihydroxy-acetone	$2.36x10^4$	$1.96x10^3$	$2.09x10^4$	$3.28x10^2$	$1.12x10^4$	$2.34x10^2$
Epichloro-hydrin	35.59	-	71.04	-	-	-
Ethylene	$1.01x10^2$	11.56	$1.03x10^2$	3.83	61.67	4.04
Ethylene Cyanohydrin	$4.51x10^4$	$3.52x10^2$	$3.89x10^4$	$5.10x10^2$	$2.04x10^4$	$3.35x10^2$

Table 4.8 (cont'd) Acute and Chronic Toxicity Concentration Values of Petroleum-Based Building Blocks for Fish, Daphnid and Green Algae

Petroleum-Based Feedstocks	ECOSAR Results					
	Organism					
	Fish		Daphnid		Green Algae	
	96-hour LC_{50} (ppm)	30-day ChV (ppm)	48-hour LC_{50} (ppm)	16-day EC_{50} (ppm)	96-hour EC_{50} (ppm)	96-hour ChV (ppm)
Ethylene Oxide	23.61	-	51.09	-	-	-
Formaldehyde	8.30	2.69	16.07	-	$4.30x10^2$	16.58
GABA	$1.09x10^6$	-	$3.91x10^4$	-	$1.07x10^4$	$6.56x10^2$
GBL	$2.24x10^2$	$4.10x10^2$	$8.65x10^3$	-	16.40	12.11
HCl	$6.20x10^2$	63.07	$6.00x10^2$	16.25	$3.45x10^2$	14.84
Ketene	$7.29x10^3$	$6.25x10^2$	$6.56x10^3$	$1.12x10^2$	$3.55x10^3$	82.66
Lactic Acid	$2.07x10^5$	$1.74x10^4$	$1.85x10^5$	$2.97x10^3$	$9.91x10^4$	$2.14x10^3$
Maleic Anhydride	$1.65x10^2$	20.05	$1.73x10^2$	7.50	$1.06x10^2$	8.48
Methyl Amine	$4.19x10^2$	-	21.98	-	16.67	2.03
Propylene	62.36	7.63	65.36	2.91	40.11	3.33
Potassium Cyanide	$1.42x10^5$	$1.00x10^4$	$1.18x10^5$	$1.20x10^3$	$5.96x10^4$	$7.06x10^2$
Succinic Anhydride	$9.75x10^2$	$1.04x10^2$	$9.62x10^2$	29.32	$5.62x10^2$	28.24
THF	$5.30x10^2$	57.57	$5.28x10^2$	17.03	$3.11x10^2$	16.83

Table 4.8 (cont'd) Acute and Chronic Concentration Values of Petroleum-Based Building Blocks for Toxicity Concern to Fish, Daphnid and Green Algae

Petroleum-Based Feedstocks	ECOSAR Results					
	Organism					
	Fish		Daphnid		Green Algae	
	96-hour LC_{50} (ppm)	30-day ChV (ppm)	48-hour LC_{50} (ppm)	16-day EC_{50} (ppm)	96-hour EC_{50} (ppm)	96-hour ChV (ppm)
Tetrahydro furfuryl alcohol	$7.29x10^3$	$6.68x10^2$	$6.75x10^3$	$1.38x10^2$	$3.74x10^3$	$1.10x10^2$
Trimethylene cyanide	$7.17x10^3$	$6.54x10^2$	$6.62x10^3$	$1.33x10^3$	$3.66x10^3$	$1.06x10^2$

The concentration values listed in Table 4.8 are classified with respect to toxicity concern of the petrochemical raw materials and reported in Table 4.9.

Table 4.9 Toxicity Classification of Petroleum-based Building Blocks

Toxicity Concern of petroleum-based building blocks		
Low Toxicity	**Moderate Toxicity**	**High Toxicity**
Acetic Acid	Acrolein	Acrylonitrile
Acetylene	1, 3 Butadiene	Allyl Alcohol
Ammonia	Epichlorohydrin	
Butane 1,2,4 triol	Ethylene	

Table 4.9 (cont'd) Toxicity Classification of Petroleum-based Building Blocks

Toxicity Concern of petroleum-based building blocks		
Low Toxicity	**Moderate Toxicity**	**High Toxicity**
Citric Acid	Ethylene Oxide	
Cyanoacetic Acid	Formaldehyde	
Dihydroxyacetone	GBL	
GABA	HCl	
Ethylene Cyanohydrin	Methyl Amine	
Ketene	Propylene	
Lactic Acid		
Maleic Anhydride		
Potassium Cyanide		
Succinic Anhydride		
Tetrahydro-furfuryl alcohol		
THF		
Trimethylene Cyanide		

It can be seen in Table 4.9 that, acrylonitrile and allyl alcohol possesses a high toxicity potential. The remaining petrochemical raw materials are either less or moderately toxic. When the toxicity potential of biological and petrochemical raw materials is compared, bio-based building blocks seem more environmentally benign. From the sustainability point of view, biological raw materials are renewable in addition being more environmentally friendly.

Products with a moderate toxicity potential are given in Table 4.10. The remaining products possess low toxicity potential except acrylonitrile, which is a derivative of 3- Hydroxypropionic acid with a high toxicity potential.

Table 4.10 Products Possessing Moderate Toxicity Concern

The products having moderate toxicity concern		
Glycerol carbonate	Aspartic anhydride	Angelilactones
Glycidol	2 methyl 1,4 BDA	Diphenolic acid
Ethyl-3HP	3 methyl pyrrolidone	1,4 diaminobutane
Methyl acrylate	5 amino1butanol	DBE
Propiolactone	Epoxy-lactone	GBL
Prolinol	G-butenyl-lactone	THF
3 amino THF	G-valerolactone	2,5 dihydroxymethylfuran
2,5 furandicarbaldehyde	Acrylate-lactone	

As shown earlier in case of a release, products are present mainly in water and soil phases and from these results it is indicated that toxic behaviors of the chemicals in water may be harmful to aquatic organisms even with a short-term exposure. The overall results of the persistence in air and aquatic toxicity of all building blocks and products are given in Figures 4.20 & 4.21. It can be seen in Figure 4.20 that, approximately 25 % of the bio-based building blocks and 52 % of the petroleum-based raw materials are highly persistent in air. Additionally, it can be seen Figure 4.21 that, all the bio-based raw materials have a low toxicity potential in aquatic medium; whereas 7 % of the petroleum-based raw materials are highly toxic, 34 % are moderately toxic and 59 % are of low toxic. Hence, the environmental criteria evaluation at the conceptual design stage support the use of bio-based feedstocks due to less persistent and toxic behavior of the feedstocks.

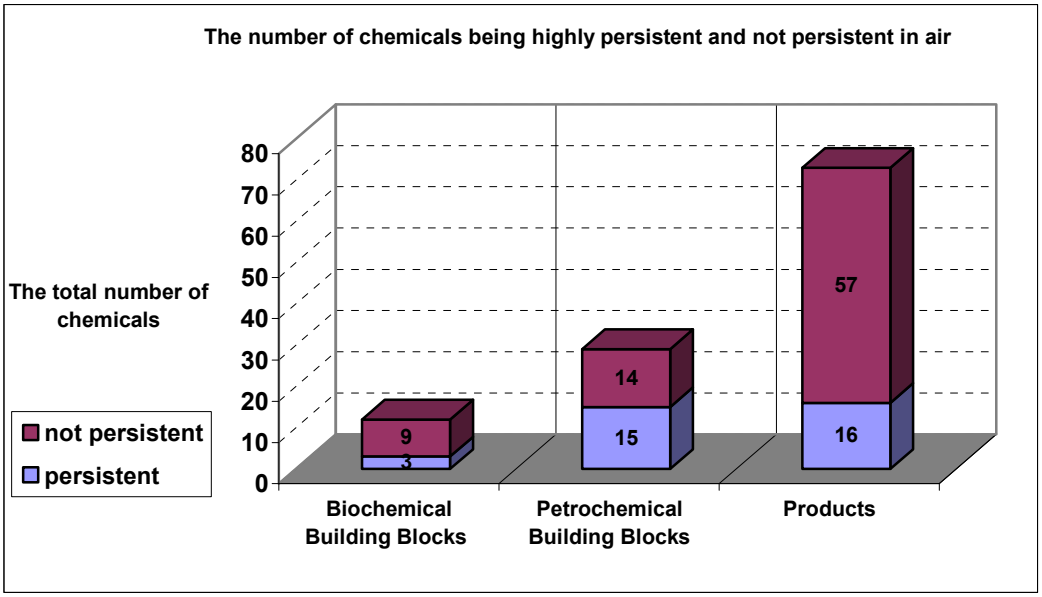

Figure 4.20 Overall Evaluation of Persistence of Building Blocks and Products in Air

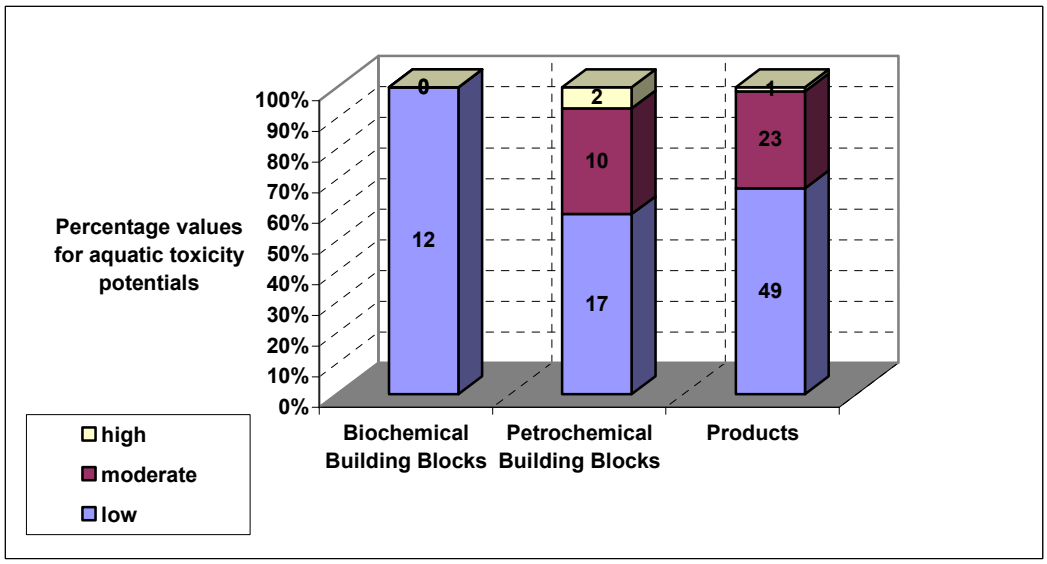

Figure 4.21 Overall Evaluation of Toxicity of Building Blocks and Products in Aqueous Medium

4.4 Comparison of the Biochemical and Petrochemical Production Routes With Respect to Persistence and Toxicity Evaluations

Conventional production routes for the products which are listed in Appendix A are compared with the alternative routes considering persistence and toxicity of raw materials. Since all raw materials are classified as having low potential to accumulate in the tissues of the living organisms, bioaccumulation of the raw materials is not considered as a comparison parameter.

In Table 4.11, acrylonitrile production routes are compared. The persistence of ammonia can not be estimated by the software. Among the four routes, the production of acrylonitrile from 3-HPA is preferable from both persistence and toxicity point of view in comparison to petrochemical ones. Both of the petrochemical routes may be regarded as having a moderate toxicity concern. From a persistence point of view, ammoxidation route is preferable to oxidation of ethylene route among the petrochemical routes.

Table 4.11 Comparison of the Persistence and Toxicity Results for Acrylonitrile Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Ammoxidation of propylene	Ammonia	Not estimated	Low
	Propylene	Not persistent in air	Moderate
Oxidation of ethylene	Ethylene	Highly persistent in air	Moderate
From 3-HPA	3-HPA	Not persistent in air	Low

Table 4.12 presents persistence and toxicity assessments for acrylamide production processes. Acrylonitrile is highly toxic and has a high potential to stay in air. Therefore, this route is rather risky for acrylamide production if the environmental impact of the process is considered.

Table 4.12 Comparison of the Persistence and Toxicity Results for Acrylamide Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Hydrogenation of acrylonitrile	Acrylonitrile	Highly persistent in air	High
From 3-HPA	3-HPA	Not persistent in air	Low

Table 4.13 reports the comparison of malonic acid production processes. Moderate toxic behavior of hydrochloric acid makes the biochemical route more attractive.

Table 4.13 Comparison of the Persistence and Toxicity Results for Malonic Acid Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Hydrolysis of cyanoacetic acid with hydrochloric acid	Cyanoacetic acid	Not persistent in air	Low
	Hydrochloric acid	Not estimated	Moderate
From 3-HPA	3-HPA	Not persistent in air	Low

In Tables 4.14-4.27, production processes for propylene glycol, acrylic acid, ethylene glycol, gamma-butyrolactone, tetrahydrofuran, N-methyl pyrrolidone, 2-pyrrolidone, 1,4 butanediol, succinic acid, glutaric acid, 1,5 pentanediol, 3-methyl THF, 3-hydroxy tetrahydrofuran and glycerol are given.

Petrochemical raw materials possess either high persistence in air or moderate toxicity potentials; whereas biochemical raw materials for propylene glycol production are less toxic and not persistent.

Table 4.14 Comparison of the Persistence and Toxicity Results for Propylene Glycol Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Hydrolysis of propylene	Propylene	Not persistent in air	Moderate
Hydrogenation of dihydroxyacetone	Dihydroxyacetone	Highly persistent in air	Low
Catalytic hydrogenation of lactic acid	Lactic acid	Highly persistent in air	Low
Dehydration & Hydrogenation of glycerol	Glycerol	Not persistent in air	Low
Hydrogenation and dehydration of sorbitol	Sorbitol	Not persistent in air	Low
Hydrogenolysis of xylitol	Xylitol	Not persistent in air	Low

Among the acrylic acid production routes, acrylonitrile route is least environmentally benign and both biochemical routes are environmentally friendly.

Table 4.15 Comparison of the Persistence and Toxicity Results for Acrylic Acid Production Processes

Processing Route	Main Raw Material	Persistence in air	Aquatic Toxicity
Oxidation of acrolein	Acrolein	Not persistent	Moderate
Carbonylation of acetylene	Acetylene	Highly persistent in air	Low

Table 4.15 (cont'd) Comparison of the Persistence and Toxicity Results for Acrylic Acid Production Processes

Processing Route	Main Raw Material	Persistence in air	Aquatic Toxicity
Hydrolysis of acrylonitrile	Acrylonitrile	Highly persistent in air	High
From ethylene cyanohydrin	Ethylene cyanohydrin	Not persistent	Low
Reaction of ketene and formaldehyde	Ketene	Not persistent	Low
	Formaldehyde	Not persistent	Moderate
Oxidation of 3- HPA	3-hydroxypropionic acid	Not persistent	Low
From levulinic acid	Levulinic acid	Not persistent	Low

In Table 4.16, ethylene oxide and ethylene are highly persistent in air and moderately toxic; whereas biochemical raw materials are not persistent and less toxic. Therefore, biochemical routes are greener in comparison to the petrochemical routes.

For products shown in Tables 4.17, 4.24-4.26, all routes equally acceptable as they show low persistence and toxicity.

Table 4.16 Comparison of the Persistence and Toxicity Results for Ethylene Glycol Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Liquid phase hydrogenation of ethylene oxide	Ethylene oxide	Highly persistent in air	Moderate
Oxidation of ethylene	Ethylene	Highly persistent in air	Moderate
Hydrogenation of glycerol	Glycerol	Not persistent in air	Low
Hydrogenolysis of xylitol	Xylitol	Not persistent in air	Low

Table 4.17 Comparison of the Persistence and Toxicity Results for Gamma-Butyrolactone Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Dehydrogenation of gamma-butyric acid	GABA	Not persistent in air	Low
Oxidation of tetrahydrofuran	THF	Not persistent in air	Low
Hydrogenation of maleic anhydride	Maleic anhydride	Highly persistent in air	Low
Hydrogenation and dehydration of succinic acid	Succinic acid	Highly persistent in air	Low

Table 4.18 Comparison of the Persistence and Toxicity Results for Tetrahydrofuran Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Dehydration of 1,4 butanediol	1,4 butanediol	Not persistent in air	Low
Hydrogenation and dehydration of succinic acid	Succinic acid	Highly persistent in air	Low

Among the N-methyl pyrrolidone production routes, the toxic behavior of the petrochemical raw materials is higher than that of the biochemical one.

Table 4.19 Comparison of the Persistence and Toxicity Results for N-methyl Pyrrolidone (NMP) Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Reaction of GBL with methyl amine	GBL	Highly persistent in air	Moderate
	Methyl amine	Not persistent in air	Moderate
From succinic acid	Succinic acid	Highly persistent in air	Low

Table 4.20 Comparison of the Persistence and Toxicity Results for 2-pyrrolidone Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Reaction of ammonia and GBL	GBL	Highly persistent in air	Moderate
	Ammonia	Not persistent in air	Low

Table 4.20 (cont'd) Comparison of the Persistence and Toxicity Results for 2-Pyrrolidone Production Processes

Hydrolysis and hydrogenation of succinonitrile	Succinonitrile	Highly persistent in air	Low
From succinic acid	Succinic acid	Highly persistent in air	Low

Petrochemical production processes for 1,4 butanediol are more toxic than the biochemical ones.

Table 4.21 Comparison of the Persistence and Toxicity Results for 1,4 Butanediol Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Reaction of Acetylene with Formaldehyde	Acetylene	Highly persistent in air	Low
	Formaldehyde	Not persistent in air	Moderate
Oxidative acetoxylation of 1, 3 Butadiene	1,3 Butadiene	Not persistent in air	Moderate
Reaction of Propylene and Acetic Acid	Propylene	Not persistent in air	Moderate
	Acetic Acid	Highly persistent in air	Low
Hydroformylation of Allyl Alcohol	Allyl Alcohol	Not persistent in air	High
Direct hydrogenation of Maleic Anhydride	Maleic Anhydride	Highly persistent in air	Low
From Succinic Acid	Succinic Acid	Highly persistent in air	Low

Table 4.22 Comparison of the Persistence and Toxicity Results for Succinic Acid Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Catalytic hydrogenation of Maleic Anhydride	Maleic Anhydride	Highly persistent in air	Low
From 2,5 FDCA	2,5 FDCA	Not persistent in air	Low

Raw materials for succinic acid production are comparable in terms of their persistence.

Table 4.23 Comparison of the Persistence and Toxicity Results for Glutaric Acid Production Processes

Processing Route	Main Raw Material	Persistence	Toxicity
Reaction of Trimethylene Cyanide with Hydrochloric Acid	Trimethylene Cyanide	Highly persistent in air	Low
	HCl	Not estimated	Moderate
Reaction of GBL with KCN and HCl	GBL	Not persistent in air	Moderate
	KCN	Highly persistent in air	Low
From Glutamic Acid	Glutamic Acid	Not persistent in air	Low

Petrochemical raw materials for glutaric acid production have a higher persistence in air and a higher toxicity potential compared to those of biochemical one.

Table 4.24 Comparison of the Persistence and Toxicity Results for 1,5 Pentanediol Production Processes

Processing Route	Main Raw Material	Persistence	Toxicity
Hydrolysis of Tetrahydrofurfuryl Alcohol	Tetrahydrofurfuryl Alcohol	Not persistent in air	Low
From Glutamic Acid	Glutamic Acid	Not persistent in air	Low

Table 4.25 Comparison of the Persistence and Toxicity Results for 3-Methyl THF Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Hydrogenation of Citric Acid	Citric Acid	Not persistent in air	Low
From Levulinic Acid	Levulinic Acid	Not persistent in air	Low

Table 4.26 Comparison of the Persistence and Toxicity Results for 3-Hydroxy Tetrahydrofuran Production Processes

Processing Route	Main Raw Material	Persistence	Aquatic Toxicity
Catalytic Dehydration of Butane 1,2,4 triol	Butane 1,2,4 triol	Not persistent in air	Low
From 3-hydroxybutyrolactone	3-hydroxybutyrolactone	Not persistent in air	Low

Table 4.27 Comparison of the Persistence and Toxicity Results for Glycerol Production Processes

Processing Route	Main Raw Material	Persistence	Toxicity
Hydrogenation of sorbitol	Sorbitol	Not persistent in air	Low
Hydrolysis of epichlorohydrin	Epichlorohydrin	Not persistent in air	High

4.5 Evaluation of the Economical Potentials of Alternative Production Routes

Biochemical feedstocks for which market price information are provided in the literature are succinic acid, glycerol and sorbitol. Utilizing the bio-based and petrochemical feedstocks and product prices, economical potential of the production routes for propylene glycol, gamma-butyrolactone, ethylene glycol, tetrahydrofuran and 1,4 butanediol are calculated.

4.5.1 Propylene Glycol Production

Propylene glycol is commercially produced from oxidation of propylene. Alternatively, this chemical can be produced from hydrogenation of glycerol and of sorbitol. Chemicals which are involved in the three processes are shown in Table 4.28 together with their 2002 market prices. Utilizing the market prices and the reaction stoichiometry, the modified economical potential values of the processes (excluding the manufacturing costs) are calculated and reported in Table 4.29.

When the economical potential of the production routes is examined, oxidation of propylene and hydrogenation of sorbitol routes seem economically feasible. Glycerol route is not economical due to high price of glycerol in 2002. If the market price of glycerol is lower than $ 0.78/ kg, glycerol route might become feasible.

Table 4.28 Technical Grade Market Price Information of Raw Materials and Products Involved in Propylene Glycol Production Processes

Chemicals	Market Price
Propylene Glycol	$1.057/kg
Propylene	$ 0.424/kg
Glycerol (99.7 wt%)	$1.320/kg
Sorbitol (70 wt% aq)	$ 0.771/kg
Hydrogen	$ 4.360 /kg
Oxygen	$0.137 /kg

Table 4.29 Economical Potential of Propylene Glycol Production Processes

Production process	Economical potential of the route
Oxidation & hydrolysis of propylene	$0.798/kg
Hydrogenation of glycerol	<0
Hydrogenation of sorbitol	$0.682/kg

4.5.2 Gamma-Butyrolactone Production

Gamma-butyrolactone might be produced from oxidation of tetrahydrofuran, hydrogenation of maleic anhydride or of succinic acid. Market price of chemicals involved in the reactions is presented in Table 4.30.

Economical potential of the petrochemical routes are feasible; whereas bio-based route is not due to the high price of succinic acid. If the succinic acid market price is lower than $ 1.99/ kg, then this route might become economically feasible.

Table 4.30 Technical Grade Market Price Information of Raw Materials and Products Involved in Gamma- butyrolactone Production Processes

Chemicals	Market Price
Gamma- Butyrolactone	$3.968/kg
Tetrahydrofuran	$2.932/kg
Maleic Anhydride	$0.838/kg
Succinic Acid	$ 5.436/kg
Hydrogen	$4.360 /kg
Oxygen	$0.137 /kg

Table 4.31 Economical Potential of Gamma-butyrolactone Production Processes

Production process	Economical potential of the route
Oxidation of tetrahydrofuran	$ 1.467/kg GBL
Hydrogenation of maleic anhydride	$ 2.966/kg GBL
Hydrogenation of succinic acid	<0

4.5.3 Ethylene Glycol Production

Ethylene glycol is commercially produced from hydrolysis of ethylene oxide and alternatively might be produced by hydrogenation of glycerol.

Market price information and economical potential of the production routes are given in Tables 4.32 & 4.33.

Hydrogenolysis of glycerol route is not economically feasible due to high glycerol prices. If the market price falls to $ 0.74/ kg of glycerol, then this production route might be feasible.

Table 4.32 Technical Grade Market Price Information of Raw Materials and Products Involved in Ethylene Glycol Production Processes

Chemicals	Market Price
Ethylene glycol	$ 1.101/kg
Ethylene oxide	$ 1.257/kg
Glycerol	$ 1.320/kg

Table 4.33 Economical Potential of Ethylene Glycol Production Processes

Production process	Economical potential of the route
Hydrolysis of ethylene oxide	$ 0.298/kg ethylene glycol
Hydrogenolysis of glycerol	<0

4.5.4 Tetrahydrofuran Production

Tetrahydrofuran might be produced from dehydration of 1,4 butanediol or hydrogenation & dehydration of succinic acid.

The succinic acid route is not economically feasible. If the price of the succinic acid falls below $ 1.49/kg succinic acid, then this route might become economically feasible.

Table 4.34 Technical Grade Market Price Information of Raw Materials and Products Involved in Tetrahydrofuran Production Processes

Chemicals used in production processes	Market Price of the chemical
Tetrahydrofuran	$2.932/kg
1,4 butanediol	$2.203/kg

Table 4.34 (cont'd) Technical Grade Market Price Information of Raw Materials and Products Involved in Tetrahydrofuran Production Processes

Succinic acid	$5.436/kg
Hydrogen	$4.360/kg

Table 4.35 Economical Potential of Tetrahydrofuran Production Processes

Production process	Economical potential of the route
Dehydration of 1,4 butanediol	$0.178/kg THF
Hydrogenation and dehydration of succinic acid	<0

4.5.5 1,4 Butanediol Production

1,4 butanediol is commercially produced from the reaction of acetylene and formaldehyde or direct hydrogenation of maleic anhydride. The bio-based production route of 1,4 butanediol is the hydrogenation & dehydration of succinic acid.

The market price information of the raw materials and the desired product are provided in Table 4.36. Together with reaction stoichiometry, the economical potentials of the production routes are calculated and presented in Table 4.37.

As it can be seen in Table 4.37, petrochemical routes are economically feasible. Succinic acid route is not competitive with the petrochemical ones. If the succinic acid price is lower than $ 1.386 / kg, then the production route might become economically feasible.

Table 4.36 Technical Grade Market Price Information of Raw Materials and Products Involved in 1,4 Butanediol Production Processes

Chemicals	Market Price
1,4 Butanediol	$2.203/kg
Acetylene	$1.808/kg
Formaldehyde	$0.4/kg
Maleic Anhydride	$0.838/kg
Succinic Acid	$ 5.436/kg
Hydrogen	$4.360/kg

Table 4.37 Economical Potential of 1,4 Butanediol Production Processes

Production process	Economical potential of the route
Reaction of acetylene with formaldehyde	$1.416/kg 1,4 BDO
Direct hydrogenation of maleic anhydride	$ 0.927/kg 1,4 BDO
Dehydration & hydrogenation of succinic acid	<0

4.6 Evaluation of Atom and Mass Efficiency of Biochemical and Petrochemical Production Routes

Atom and mass efficiency results of the processes considered in the economical analysis evaluations are presented in Tables 4.38- 4.39.

In Table 4.38, it is observed that atom and mass efficiency of the petrochemical process are higher than the bio-based ones. This is because petrochemical route is an addition reaction and glycerol and sorbitol routes are elimination and substitution reactions subsequently.

Table 4.38 Atom and Mass Efficiency of Propylene Glycol Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Oxidation & hydrolysis of propylene	100	100	100	-	100 %
Hydrogenation & dehydration of glycerol	100	80	67	-	81 %
Hydrogenation & dehydration of sorbitol	100	80	67	-	81 %

Table 4.39 Atom and Mass Efficiency of GBL Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Oxidation of THF	100	75	67	-	83 %
Hydrogenation of Maleic Anhydride	100	100	67	-	84 %
Hydrogenation of Succinic Acid	100	60	50	-	70 %

As it can be seen from Table 4.39 that atom and mass efficiency of petrochemical processes is higher than bio-based route. This is because petrochemical routes involve substitution reactions; whereas the bio-based route is an elimination reaction.

Table 4.40 Atom and Mass Efficiency of Ethylene Glycol Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Hydrolysis of Ethylene Oxide	100	100	100	-	100 %
Hydrogenolysis of Glycerol	67	75	67	-	67 %

Table 4.41 Atom and Mass Efficiency of Tetrahydrofuran Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Dehydration of 1,4 butanediol	100	80	50	-	80 %
Hydrogenation and dehydration of succinic acid	100	57	25	-	57 %

Production routes of ethylene glycol production processes are provided in Table 4.40. The petrochemical route involves an addition reaction; whereas the bio-based one is an elimination reaction. Therefore, efficiency of the bio-based process is less than that of petrochemical one.

In Table 4.41, petrochemical production process of tetrahydrofuran seems more efficient than bio-based one. Although petrochemical process is an elimination reaction and bio-based one is substitution reaction, bio-based one produces 3 times more amount of water than the petrochemical one. Therefore, atom and mass efficiency of bio-based one is lower than that of petrochemical one.

Acetylene and formaldehyde reaction for 1,4 butanediol production is the most efficient process due to it is an addition reaction. The reason of having lower efficiency values for maleic anhydrideand succinic acid routes is that the reactions are substitution elimination reactions subsequently.

Table 4.42 Atom and Mass Efficiency of 1,4 Butanediol Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Reaction of acetylene with formaldehyde	100	100	100	-	100 %
Direct hydrogenation of maleic anhydride	50	42	40	-	85 %
Dehydration & hydrogenation of succinic acid	100	71	50	-	76%

Atom and mass efficiency results of acrylic acid production processes are provided in Table 4.43. In Table 4.43, it is observed that the catalytic carbonyl reaction (acetylene with carbonmonoxide and water) and oxidation of acrolein give the most efficient results due to the nature of the involved reactions are addition reactions. Second ranking are the biological production routes, lactic & 3-Hydroxypropionic acid and the propylene route which exhibit reasonable efficiency. The remaining routes are less efficient than the biochemical routes. Additionally, the by-products of the least efficient routes are ammonium compounds; whereas biological routes and propylene route produces water as a by-product.

Table 4.43 Atom and Mass Efficiency of Acrylic Acid Production Routes

Production Route	Atom efficiency (%)				Mass efficiency
	C	H	O	N	
Catalytic Carbonyl Reaction	100	100	100	-	100 %
Dehydration of Lactic Acid	100	67	67	-	80 %
Ethylene Cyanohydrin	100	44	33	0	39 %
Hydrolysis of Acrylonitrile	100	31	25	0	52 %
Oxidation of Propylene	67	67	67	-	80 %
Oxidation of Acrolein	100	100	100	-	100 %
Dehydration & Oxidation of 3-HPA	100	67	67	-	80 %

In Table 4.44, atom and mass efficiency of various biochemical production processes are summarized. Commercial petrochemical based routes are not available in the literature. It is seen that except glycidol production from glycerol, remaining routes are quite efficient.

Table 4.44 Atom and Mass Efficiency of Various Biochemical Production Routes

Derivative Name	**Raw material**	**Atom Efficiency (%)**					**Mass Efficiency**
		C	**H**	**O**	**N**		
Angelilactone	Levulinic Acid	100	75	67	-	-	85%
γ-valerolactone	Levulinic Acid	100	80	67	-	-	86%
1,4 pentanediol	Levulinic Acid	100	86	67	-	-	85%
DALA	Levulinic Acid	63	47	50	100	0(Br)	68%

Table 4.44 (cont'd) Atom and Mass Efficiency of Various Biochemical Production Routes

Glycerol Carbonate	Glycerol	67	43	67	-	-	65%
Glycidol	Glycerol	50	43	33	-	-	41 %
Glyceric Acid	Glycerol	100	63	100	-	0(Na)	80 %

4.7 The Relationship between the Gibbs Free Energy of Major Reactions of Processes and the Economical Potential

The relationship between the Gibbs free energy of major reactions of commercial processes and economical potential are presented in Figure 4.22. Market price information for the chemicals in the years 1997-2005 which are used in economical analysis is given in Appendix H.

Because most of the free energy of change values of reactions is between 0 and -500 kJ/ mole, the processes with Gibbs free energy of change values in this range are provided in Figure 4.22. No correlation between the values of economical potential and free energy of change of reactions is observed. If there were a correlation, the expected trend would be an increase in economical potential with a more negative value of the free energy change. It should be noted that, Gibbs free energy of change values is calculated at standard state and economical potential values do not include purification and manufacturing costs of processes which have considerable effects on the economical potential of the production processes. Although free energy of changes of the reactions are calculated at standard state, it is observed that commercial processes have mostly negative values indicating that chemical industry pays attention to spontaneity of the reactions. Therefore, free energy of change values of the reactions still might be used as a comparison parameter for the processes.

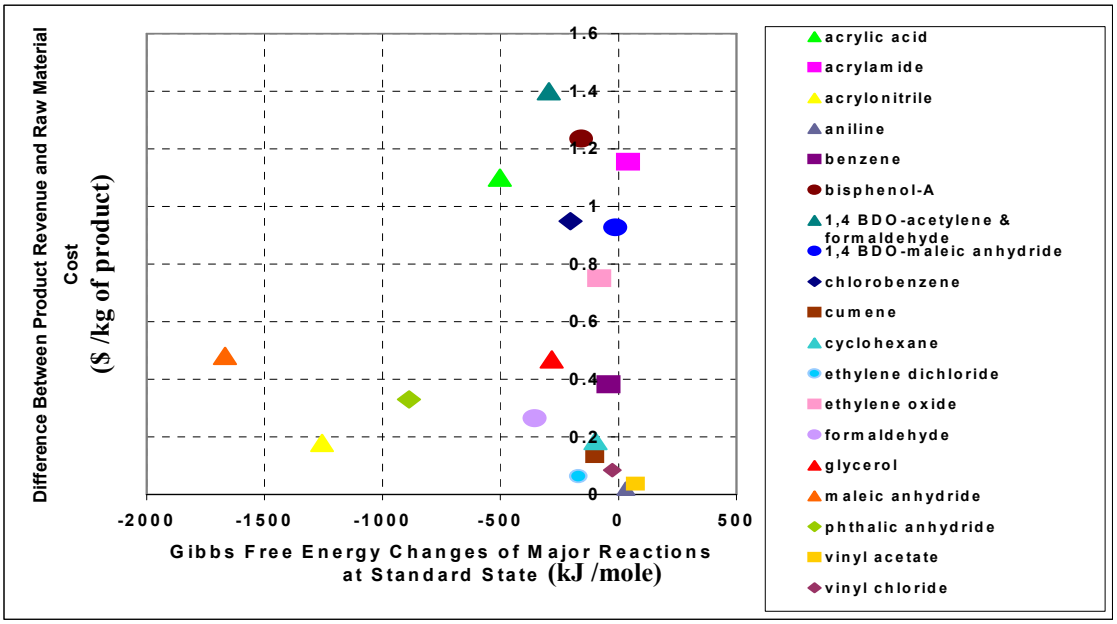

Figure 4.22 Economical Potential of Processes versus the Gibbs Free Energy Change of Major Reactions

The only opportunity is to compare the production routes for the same product namely 1,4 butanediol. The first production route is based on the reaction of acetylene and formaldehyde and the second route is on the reaction of maleic anhydride. When the two production pathways are compared, the expected relationship is observed. The first production route has a lower free energy of change of reaction value and a higher economical potential than the second route. This result suggests that probably it is more appropriate to compare different synthesis pathways for the same compound. However, it is not certain that for other products and production routes the results will be in the same direction.

4.8 Environmental Performance Evaluation at the Conceptual and Preliminary Design Stage for 1,3 Propanediol Production

4.8.1 Comparison of Environmental Performances of 1,3 Propanediol Production Processes at the Conceptual Design Stage

Petrochemical and biochemical production processes of 1,3 PDO are listed below:

- Hydration of acrolein
- Hydroformylation of ethylene oxide
- Reduction of 3-hydroxypropionic acid (HPA)
- Utilization of glycerol via microorganisms

First stage environmental criteria evaluation of processes considering the persistence and toxicity of raw materials are presented in Table 4.45. Hydroformylation of ethylene route is less environmentally benign due to high persistence of ethylene in air and its moderate aqueous toxicity. Biochemical routes give better results with respect to environmental criteria.

Table 4.45 Stage 1 Environmental Criteria Evaluation of Biochemical and Petrochemical Feedstocks of 1,3 Propanediol

Production Route	Raw Material	Persistence	Toxicity
Oxidation of acrolein	Acrolein	Not persistent in air	Moderate
Hydroformylation of ethylene oxide	Ethylene oxide	Highly persistent in air	Moderate
Reduction of 3-HPA	3-HPA	Not persistent in air	Low
Production from glycerol	Glycerol	Not persistent in air	Low

Economical analysis is performed for hydrocarbonylation of ethylene oxide and fermentation of glycerol because market price of acrolein could not be found. Additionally, the market price of 1,3 PDO in 2002 is not available. However, it is available for 1994 reported as $12-20/ lb for the technical grade (98% purity) with a market volume of less than 0.1 million lb/ year [39]. With a market volume of 10,000,000 lb/ year and $ 1.10 per lb, it is proposed to be commercialized. Since 2002 is selected as the year to perform the economical analysis, 1994 price is not used.

Instead the market price is approximated by assuming it to be equal to the production cost. In a study of Deckwer, the cost of production of 1,3 PDO by the microbial process, including product recovery and purification, is estimated by [25]:

$$\text{Price of 1,3 PDO} = 1 + 2 \times (\text{Pr}\,iceOfGlycerol) \tag{4.1}$$

Utilizing the market price approximation provided by the above equation economical analysis for the microbial production with glycerol as the raw material and ethylene oxide route can be compared. The market price of chemicals and economical potential of the production routes are presented in Tables 4.46 & 4.47.

Table 4.46 Technical Grade Market Prices of the Raw materials and Estimated Market Price of 1,3 PDO

Chemicals used in production processes	Market Price of the chemical
Ethylene oxide	$1.257/kg
Hydrogen	$4.360/kg
Glycerol	$1.320/kg
1,3 propanediol	$ 3.64/kg

Table 4.47 Economical Potential of 1,3 PDO Production Processes

Process	Economical potential
Hydroformylation of ethylene oxide	$2.42 /kg 1,3 PDO
Microbial glycerol utilization	$ 3.32 /kg 1,3 PDO

Economical potential of glycerol route is much higher than that of ethylene oxide route and extention of the design to preliminary stage is well founded.

In the next section, the second stage environmental performance of 1,3 PDO with two different microorganisms is evaluated.

4.8.2 Comparison of the Environmental Performance of 1,3 Propanediol Production Processes at the Preliminary Design Stage

Second stage criteria evaluation of the environmental performance of 1,3 propanediol processes from glycerol utilizing *Klebsiella pneumoniae* and *Clostridium butyricum* is achieved considering material and energy consumption, cooling water consumption and CO_2, SO_2, NO_X, CO emissions to the atmosphere. Calculations for the second stage environmental criteria assessment are presented in Appendix F. Block diagrams of the two processes are given in Figures 4.23.

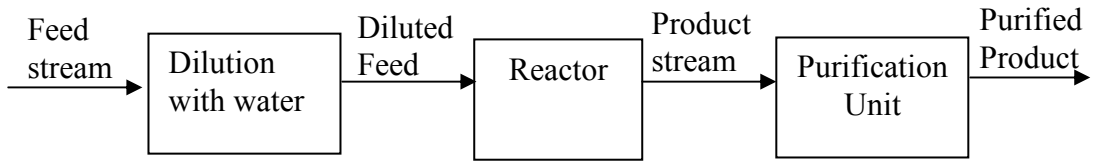

Figure 4.23 Block Diagram of 1,3 PDO Production with *Klebsiella pneumoniae* and *Clostridium butyricum*

The dilution of 70 wt % inlet glycerol to 2.9 wt% is performed in the first unit. The purification unit is for the separation of 1,3 propanediol from the product stream to 99.7 wt % 1,3 propanediol and the remaining portion is water [40]. The product stream with *Klebsiella pneumoniae* involves 1,3 propanediol, acetic acid, carbon dioxide, hydrogen and water; whereas *Clostridium butyricum* process involves 1,3 propanediol, butyric acid, carbon dioxide and water in the product stream. Both of the processes are exothermic and in order to keep the reactor temperature constant at 33 & 37 ˚C, cooling water is used. Cooling water cost is mainly due to cost of electricity consumption for pumping. Therefore, cooling water use could be linked to emissions due to electricity consumption for pumping. Using the cost of electricity per kWh, the electricity demand and emissions due to electricity usage are calculated. Additionally, purification operations in both of the processes are considered as the evaporation of mainly water and small portions of by-products. For this purpose, steam is used and energy consumption of the processes is directly related with the use of steam. Comparison of the two processes due to raw material, energy, cooling water consumption and carbon dioxide emission are provided in Table 4.48.

Table 4.48 Comparison of the two 1,3 Propanediol Processes Due to Raw Material Energy, Cooling Water Consumption and Carbon dioxide Emissions

Production Process	Raw Material Consumption (kg/ kg PDO)	Carbon Dioxide Emission (kg/ kg PDO)	Energy Consumption (kJ/ kg PDO)	CoolingWater Consumption (kg/ kg PDO)
Klebsiella pneumoniae	0.55	0.29	1.48×10^5	12.93
Clostridium butyricum	0.55	0.29	1.45×10^5	32.22

From the results in Table 4.48 it is seen that, raw material consumption and emission of carbon dioxide produced are equal for both of the processes. The order of magnitude of energy consumption values is almost same for both of the processes. The energy consumption value of the first process is slightly higher than the second one, because the reaction temperature is less than the second one and it requires more energy to remove the water. Second process needs more cooling water to keep the reaction temperature constant due to higher heat release during reactor operations. The steam and cooling water calculations are done without considering energy intensification of the processes. However, fully developed designs of the processes might consider energy intensification between the units and this might change the amount of utilities consumed in the processes. Emission of CO, CO_2, NO_X and SO_2 gases for the processes due to use of steam and electricity are given in Tables 4.49 & 4.50. When the emission of the processes due to utility usage (secondary emissions) is considered, the second route seems better due to less use of steam.

Table 4.49 Secondary Emissions of CO, CO_2, NO_X and SO_2 for Propanediol Production from Glycerol Utilizing *Klebsiella pneumoniae*

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.5×10^{-2}	6.35	8.98×10^{3}	1.06×10^{1}

Table 4.50 Secondary Emissions of CO, CO_2, NO_X and SO_2 for Propanediol Production from Glycerol Utilizing *Clostridium butyricum*

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.4×10^{-2}	6.18	8.73×10^{3}	1.03×10^{1}

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The aim of this study is to select appropriate process performance criteria to be applied at different stages of process design and to evaluate environmental performance of alternative production routes. Two significant concepts that are used for this purpose throughout the study are sustainability and green engineering. The sustainability concept mainly deals with the selection of production routes based on renewable or replaceable raw materials such as the biomass. On the other hand the green engineering concept mainly deals the application of environmental performance criteria to various stages of chemical process design.

Process performance criteria that are used in this study at the conceptual design stage are persistence, bioaccumulation, toxicity, atom and mass efficiency, economic potential of the synthesis routes and the Gibbs free energy versus the economic potential relationship.

The evaluation of persistence and bioaccumulation proved to be easier than toxicity. Toxicity evaluation is restricted to the aquatic toxicity potential of the chemicals for specific groups of organisms, namely fish, daphnid and green algae. Environmental performance results of the study can be summarized as follows:

- Biochemical and petrochemical raw materials and products considered in this study have a low bioaccumulation potential.
- In case of a release, chemicals show a major presence in soil and water compartments of the environment.

- Bio-based raw materials are not persistent in water. Of the chemicals considered in this study, succinic acid, 2,5 FDCA and levulinic acid show a high persistence in air.
- Petroleum-based raw materials are not persistent in water. Acetic acid, acetylene, acrylonitrile, citric acid, cyanoacetic acid, dihydroxyacetone, epichlorohydrin, ethylene cyanohydrin, ethylene oxide, gamma-butyrolactone, lactic acid, maleic anhydride, potassium cyanide, succinic anhydride and trimetylene cyanide are classified as being "highly persistent" in air.
- Products are not persistent in water. Within the product group, propanol, glycidol, propiolactone, acrylonitrile, glucarodilactone, 3,4 methyl gamma-butyrolactone, glutaric acid, g-valerolactone, ethylene glycol, lactic acid, DBE, GBL, succinic acid and epoxy lactone are highly persistent in air.
- Toxicity evaluation of the bio-based raw materials shows that all biological building blocks have a low toxicity potential.
- Among the petrochemical raw materials, acrylonitrile and allyl alcohol have a high toxicity potential. Acrolein, 1,3 butadiene, epichlorohydrin, ethylene, ethylene oxide, formaldehyde, gamma-butyrolactone, hydrochloric acid, methyl amine and propylene are classified as moderately toxic. The remaining petroleum-based raw materials exhibit a low toxicity potential.
- Toxicity assessment of the products reveals that among the products acrylonitrile has a high toxicity potential. Products classified in the moderately toxic group are glycerol carbonate, glycidol, ethyl-3HP, methyl acrylate, propiolactone, 3 amino THF, aspartic anhydride, 2 methyl 1,4 BDA, 3 methyl pyrrolidone, 5 amino 1 butanol, epoxylactone, g-butenyl-lactone, prolinol, g-valerolactone, angelilactones, diphenolic acid, 1,4 diaminobutane, DBE, GBL, THF, 2,5 dihydroxymethylfuran 2,5

furandicarbaldehyde and acrylate-lactone. The rest of the products exhibit a low toxicity potential in the aquatic medium.

Results of the first stage environmental criteria evaluations indicate that the renewable bio-based production routes have the additional advantage of resulting in more environmentally-benign processes in comparison to petrochemical-based ones.

Economic potential of the bio-based and petrochemical production routes for propylene glycol, gamma-butyrolactone, ethylene glycol, tetrahydrofuran and 1,4 butanediol at the conceptual design stage are compared. It is concluded that with the 2002 market price values that the bio-based routes are not as competitive as the petrochemical ones mainly due to higher prices of bio-based raw materials. If the market price of glycerol and succinic acid fall significantly in due course, the bio-based routes may become economically more attractive. In fact, glycerol price is lowered due to its production as a by-product in biodiesel industry.

Another criterion at the conceptual design stage is the atom and mass efficiency of the production routes. Atom and mass efficiencies of propylene glycol, gamma-butyrolactone, ethylene glycol, tetrahydrofuran and 1,4 butanediol are evaluated for both petrochemical and bio-based production routes. Additionally, atom & mass efficiency results for the commercial production of acrylic acid and various bio-based processes are reported. In general, petrochemical routes give better atom and mass efficiency values compared to bio-based routes. However, efficiency values of some bio-based routes are considerably higher than some of the petroleum-based ones. Hence, for some productions bio-based production routes are advantageous also in regard to this criterion.

The last criterion considered at the conceptual design stage is a presumed relationship between the Gibbs free energy of reactions versus the economical potential. In this respect, production routes of major commercial chemicals are analyzed. However, a correlation is not identified. The Gibbs free energy values of the reactions are calculated at standard state and economical potential values do not involve purification and manufacturing costs of processes which have considerable effects on the economical potential of the production processes. Although free energy of changes

of the reactions are calculated at standard state, it is observed that commercial processes have mostly negative values indicating that chemical industry pays attention to spontaneity of the reactions. Therefore, free energy of change values of the reactions still might be used as a comparison parameter for the processes.

An expected relation is observed however for the two different production routes of 1,4 butanediol. This result suggests that comparison of different synthesis pathways for the same compound might be appropriate for the relationship. However, it is not certain that for other products and production routes the results will be in the same direction.

For the production of 1,3 propanediol, in addition to the first stage criteria evaluation, an assessment is also done due to the second stage criteria of process design. Production routes of 1,3 propanediol which are considered in this study are:

- Hydration of acrolein
- Hydroformylation of ethylene oxide
- Reduction of 3-hydroxypropionic acid
- Microbial production from glycerol

Persistence evaluation of production routes shows that hydroformylation of ethylene oxide is the least environmentally friendly route, since ethylene oxide is highly persistent in air and moderately toxic in aqueous media. Acrolein route is not preferable because of moderate toxicity potential of the raw material in aqueous media. Therefore, petrochemical routes are environmentally less benign compared to bio-based ones. Additionally, economical analysis of 1,3 PDO production routes show that microbial processes are more advantageous compared to the ethylene oxide process.

Second stage metrics are evaluated for the 1,3 propanediol processes based on glycerol utilizing *Klebsiella pneumoniae* and *Clostridium butyricum*. Processes are compared with respect to their material and energy consumption, cooling water requirement and emission of CO, CO_2 (coming from the reaction stochiometry and utility use), SO_2, NO_X. Raw material consumption and the carbon dioxide produced by

the reactions are the same for both processes. On the other hand, the two microbial processes are different in their energy consumption and cooling water requirements. The energy consumption and cooling water requirement of the processes are considered without energy intensification. Energy consumption values are closely related with steam requirements of processes. The product stream of the *Klebsiella pneumoniae* process requires the removal of higher amounts of water, resulting in a higher amount of steam requirement for purification. *Clostridium butyricum* process needs more cooling water. If energy integration between units is possible for a fully-developed process of 1,3 propanediol production, then it might change the steam and cooling water requirements of the systems.

Without energy integration, *Klebsiella pneumoniae* process utilizes more energy and this causes an increase in the production cost. Since the secondary emission of processes is directly related with the use of steam and electricity, the emission of CO, CO_2, NO_X and SO_2 for the process is also higher. Therefore, without energy integration the *Clostridium butyricum* process is preferable. Additionally, pathogenic behavior of *Klebsiella pneumonia* makes this process less preferable.

This study guides the selection and utilization of process performance criteria during process development. The main idea is that process development should consider the concepts of sustainability and green engineering. This requires the incorporation of environmental performance evaluation at each stage of process design in addition to economical evaluations.

The study is performed for a wide range of chemicals hoping to provide a complete guide. Using the basic concepts and approaches considered here, more detailed analysis for specific products can be performed.

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Adipic Acid, Nitric Acid, Calcium Chloride, Nitrobenzene, Aniline, O-Xylene, Caprolactam, Cumene, Ethylene Dichloride, Sodium Sulfite, Sorbitol.

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APPENDIX A

BIO-BASED AND PETROLEUM-BASED ROUTES OF DERIVATIVES

A.1 Flowcharts Linking Commodity Chemicals to Petroleum-Based Feedstocks and Building Blocks to Bio-based Building Blocks

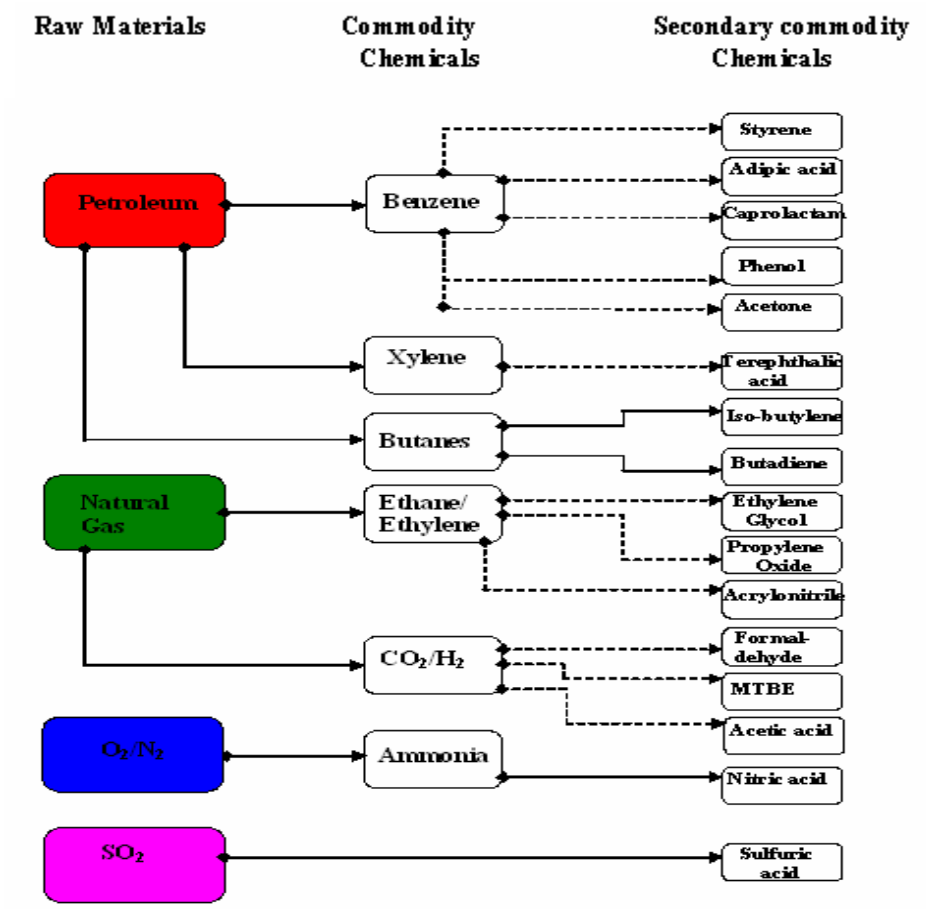


Figure A.1 A Typical Flowchart Linking Commodity Chemicals to Petroleum-Based Feedstocks [1]

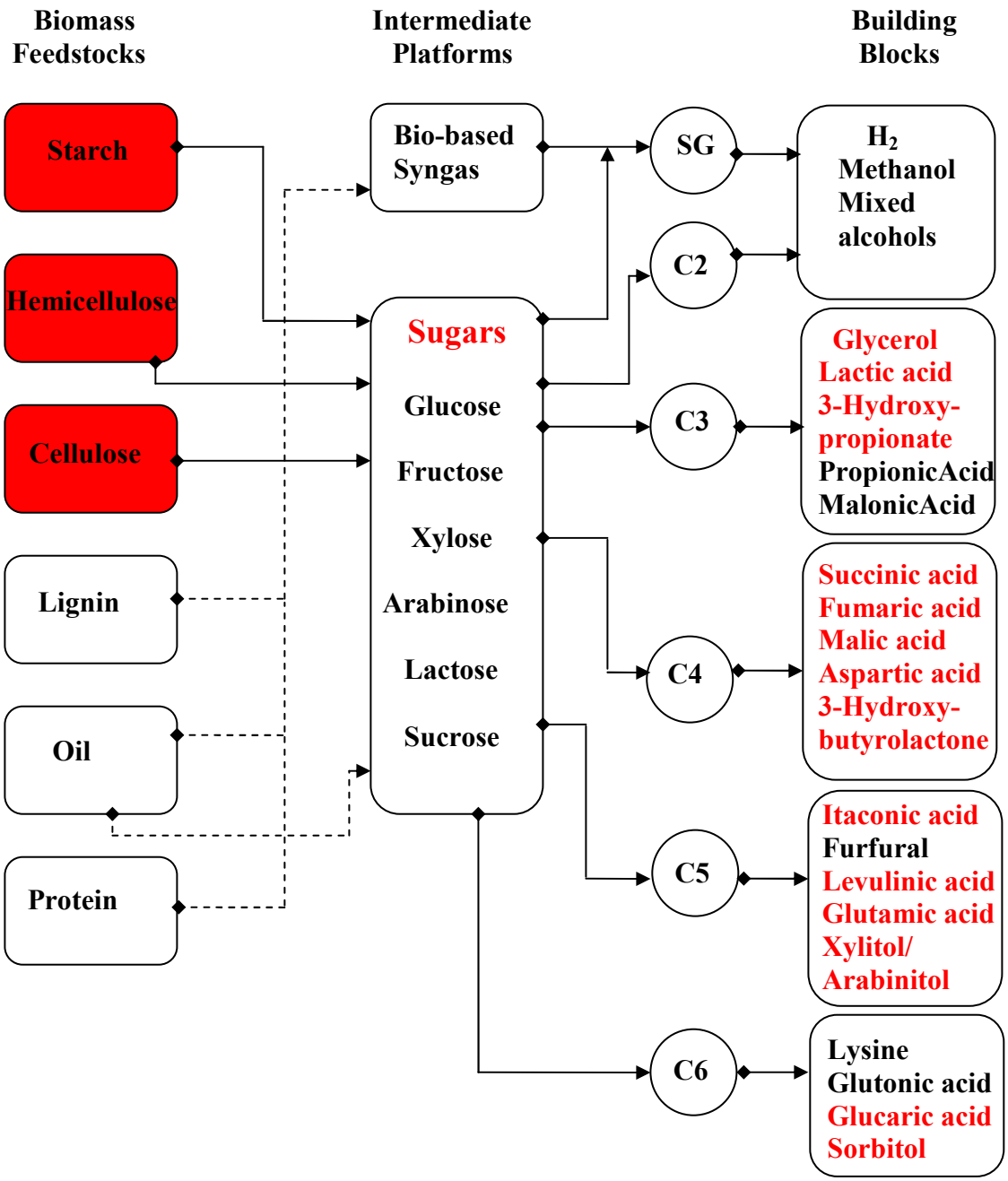


Figure A.2 A Flowchart Linking Building Blocks to Bio-Based Feedstocks [1] (SG indicates syngas; C2-C6 Indicate the carbon number)

A.2 Structural Representation of Bio-Based Building Blocks and Their Derivatives

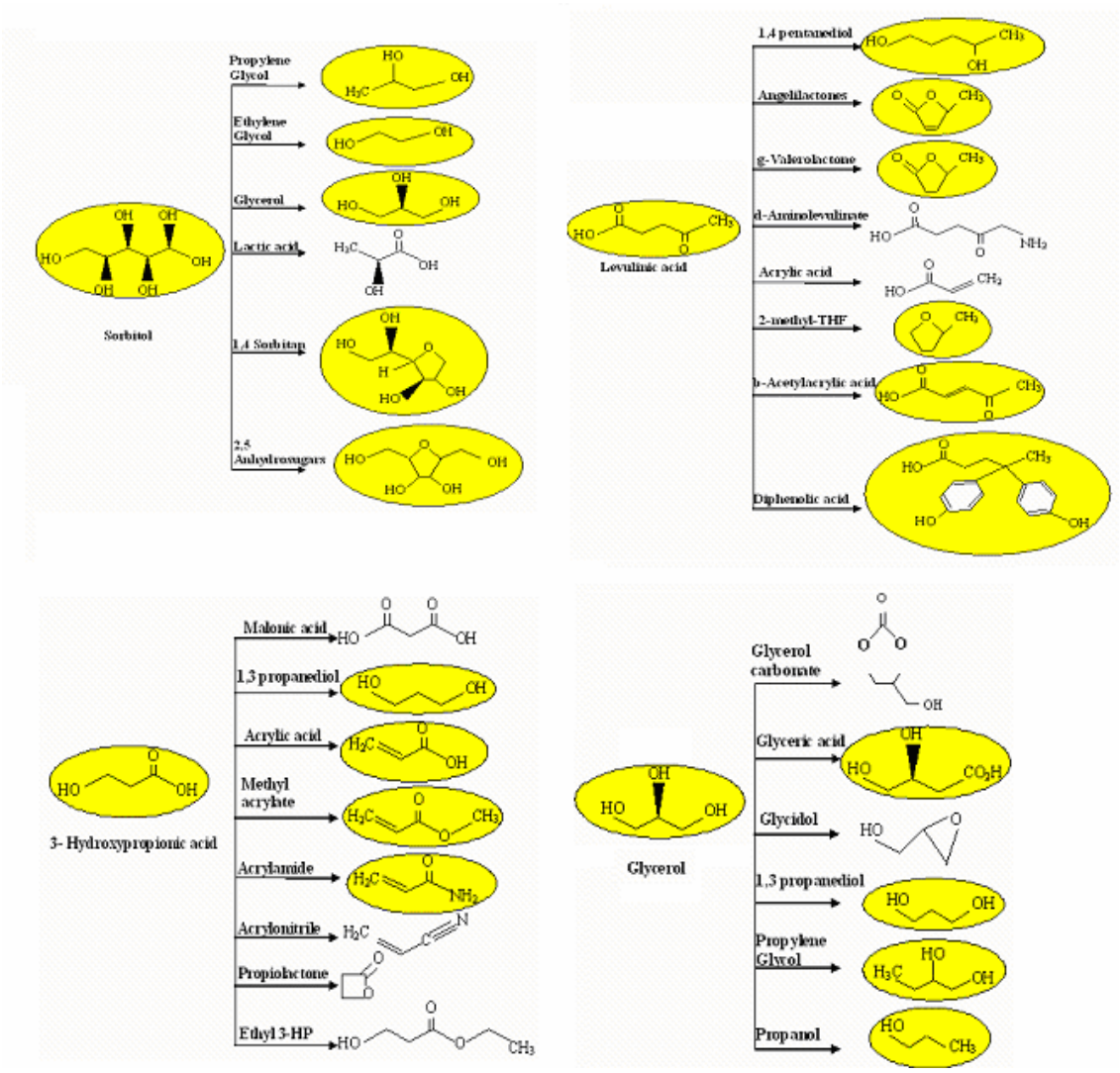


Figure A.3 Chemical Representation of Sorbitol, Levulinic Acid, 3-Hydroxypropionic Acid, Glycerol and Their Derivatives [1]

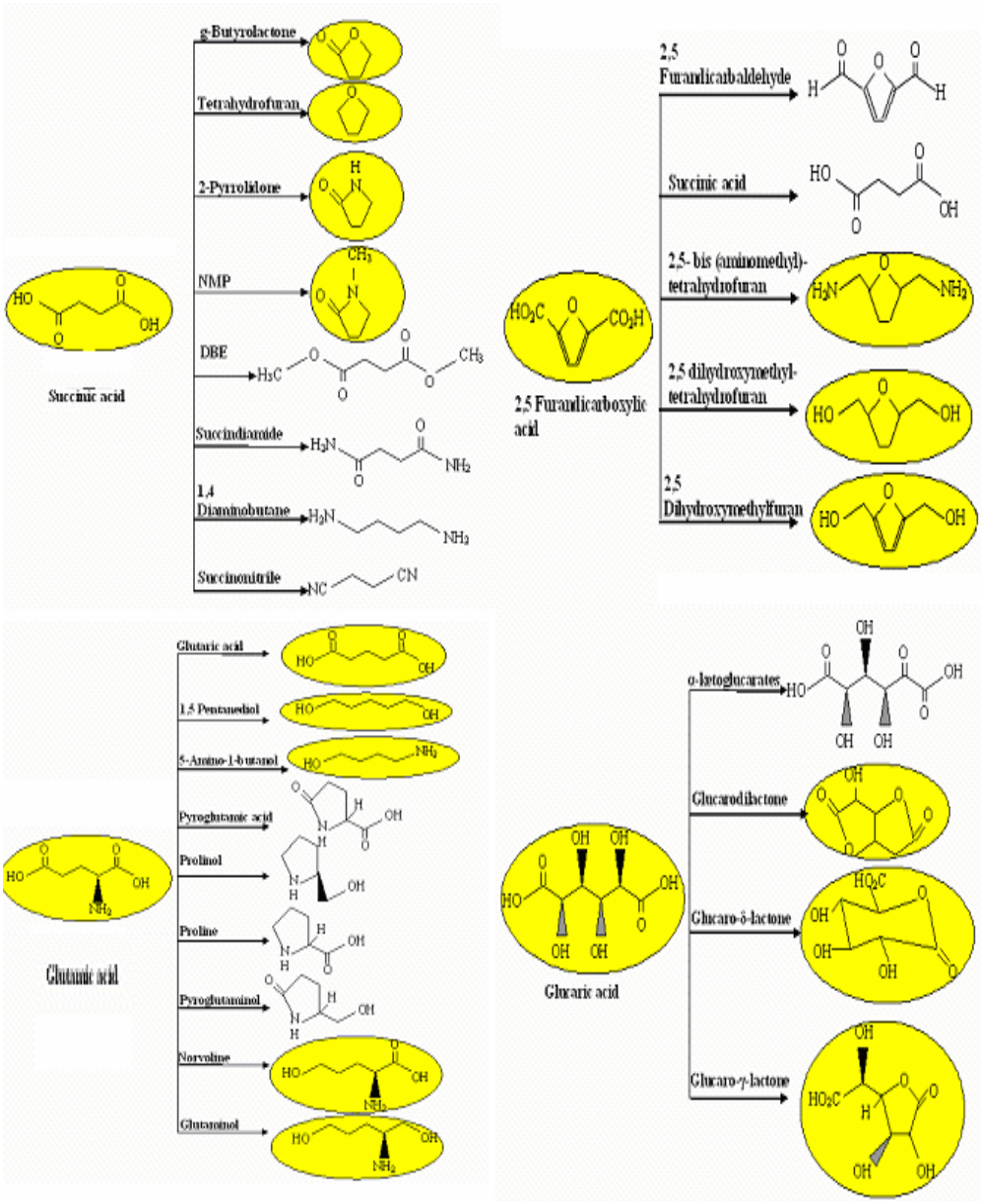


Figure A.4 Chemical Representation of Succinic, Glutamic, Glucaric Acids, 2,5 FDCA and Their Derivatives[1]

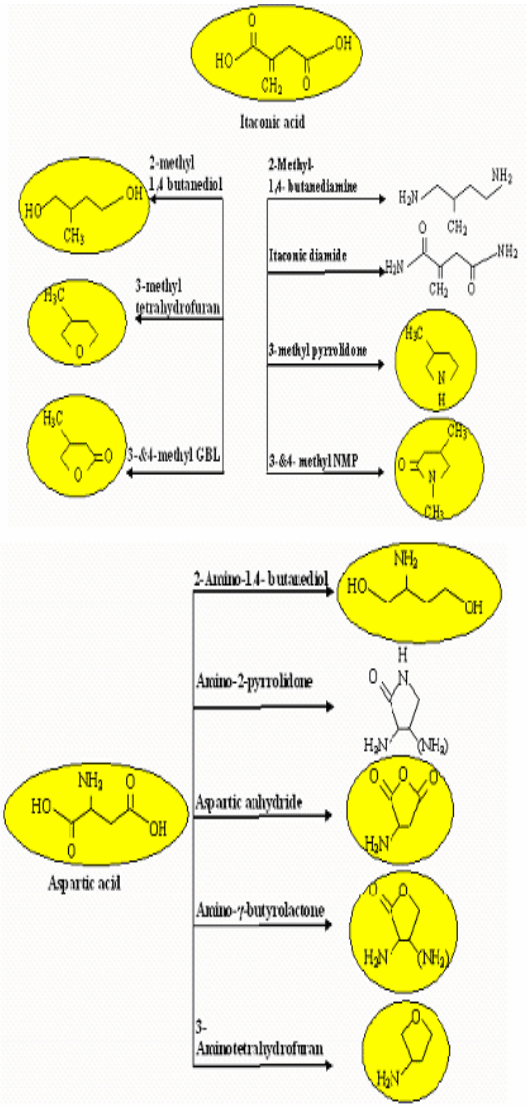


Figure A.5 Chemical Representation of Itaconic, Aspartic Acids and Their Derivatives [1]

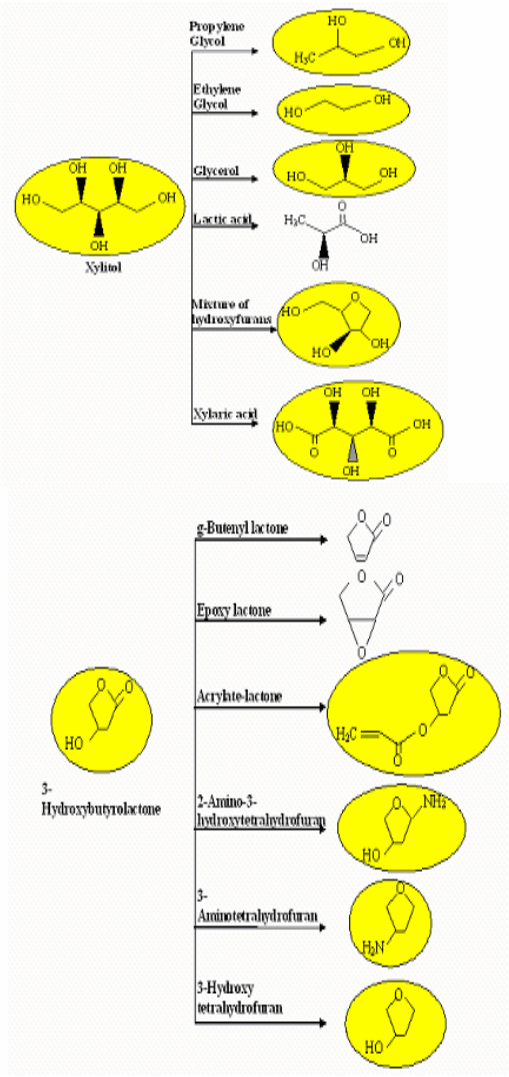


Figure A.6 Chemical Representation of Xylitol, 3-hydroxybutyrolactone and Their Derivatives [1]

A.3 Production of Building Blocks and Their Derivatives

A.3.1 Production of Glycerol and Its Derivatives

Glycerol is mainly produced as a by-product in the biodiesel industry [1]. Since biodiesel production gains importance and biodiesel production provides 10 kg of glycerol for each 90 kg of biodiesel, conversion of crude glycerol to other chemicals is important. Derivatives are produced via oxidation, hydrogenolysis and direct polymerization. Glycerol conversion to glyceric acid, glycerol carbonate, glycidol and propylene glycol are described in Table A.1.

Table A.1 Production of Glycerol Derivatives with Bio-Based Feedstocks

Derivative	Production Route
Glycerol Carbonate	• Reaction of glycerol and dimethyl carbonate [41]
Glyceric Acid	• Oxidation of glycerol with sodium hydroxide solution [25]
Glycidol	• Catalytic reaction using Zeolite-A or γ-alumina [25]
Propylene Glycol	• Dehydration & Hydrogenation of glycerol [42]
Ethylene Glycol	• Hydrogenolysis of glycerol [42]
1,3 Propanediol	• Utilization of glycerol via microorganisms[26& 38]

A.3.2 Production of 3-Hydroxypropionic Acid (3-HPA) and Its Derivatives

Conventional 3-hydroxypropionic acid (3-HPA) synthesis route is the hydration of acrylic acid or conversion of ethylene chlorohydrin with sodium cyanide [43].

The conversion of 3-HPA to 1,3 propanediol and acrylic acid are given in the literature and presented in Table A.2.

Table A.2 Bio-based Production Routes of 3-Hydroxypropionic Acid Derivatives

Derivative	Biological Production Route
1,3 Propanediol	• Reduction of 3-hydroxypropionic acid [44]
Acrylic Acid	• Oxidation of 3-hydroxypropionic acid [44]

A.3.3 Production of Levulinic Acid and Its Derivatives

Levulinic acid is produced from 6- carbon sugar carbohydrates such as starch in the presence of acid or 5-carbon sugars such as xylitol [1]. Levulinic acid may be produced with high yield and low cost from these renewable feedstocks [45]. Production routes of angelilactone, γ-valerolactone, 1,4 pentanediol, d-aminolevulinate and diphenolic acid from levulinic acid are reported in the literature and are given in Table A.3.

Table A.3 Production Routes of Levulinic Acid Derivatives

Derivative	Biological Production Route
Angelilactone	• Dehydration of levulinic acid [45]
γ-Valerolactone	• Dehydration and reduction of levulinic acid [45]
1,4 Pentanediol	• Hydrogenation of γ-valerolactone [45]
d-Aminolevulinate	• Bromination and amination of levulinic acid [45]
Diphenolic acid	• Reaction of levulinic acid with phenol [45]

A.3.4 Production of Sorbitol and Its Derivatives

Sorbitol is produced from hydrogenation of glucose using a Raney nickel type catalyst.

Production routes of glycerol, propylene glycol and isosorbide from sorbitol are given in the literature and reported in Table A.4.

Table A.4 Bio-based Production Routes of Sorbitol Derivatives

Derivative	Biological Production Route
Glycerol	• Hydrogenation of sorbitol [46]
Propylene Glycol	• Hydrogenation and dehydration of sorbitol [46]
Isosorbide	• Dehydration of sorbitol [47]

A.3.5 Production of Succinic Acid and Its Derivatives

Succinic acid is produced from fermentation of glucose.

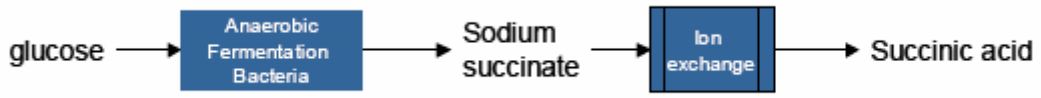


Figure A.7 Production of Succinic Acid from Glucose [1]

Production of gamma-butyrolactone, tetrahydrofuran and 1, 4 butanediol are reported in the literature and presented in Table A.5.

Table A.5 Production Routes of Succinic Acid Derivatives

Derivative	Biological Production Route
Gamma-Butyrolactone	• Hydrogenation and dehydration of maleic anhydride [48&49]
Tetrahydrofuran	• Hydrogenation and dehydration of succinic acid [49]
1,4 butanediol	• Hydrogenation and dehydration of succinic acid [49]

A.3.6 Production of 2,5 Furan Dicarboxylic Acid (FDCA) and Its Derivatives

2, 5 furan dicarboxylic acid (FDCA) is produced from oxidative dehydration of glucose [1]. Production routes of 2,5 FDCA derivatives are not reported in the literature.

A.3.7 Production of Glutamic Acid and Its Derivatives

Glutamic acid is produced from fermentation of sugars. It is reported in the literature that the major production mechanism of glutamic acid derivatives is reduction.

A.3.8 Production of Glucaric Acid and Its Derivatives

Glucaric acid is produced from glucose with oxidation of nitric acid [1]. For glucaric acid derivatives neither biochemical nor petrochemical production routes are reported in the literature.

A.3.9 Production of Aspartic Acid and Its Derivatives

L-aspartic acid is the most common type of aspartic acid reported in the literature. The preferred production method for L-aspartic acid is the reaction of ammonia with fumaric acid in the presence of lyase enzyme. Conversion of aspartic acid to its derivatives requires direct fermentation of sugars. However, this route is not competitive with the existing routes due to its high cost [1].

A.3.10 Production of Itaconic Acid and Its Derivatives

Production of itaconic acid is reported in the literature as fermentation of carbohydrates using fungi as the microorganism [50]. Conversion of itaconic acid to its derivatives is not exactly known, but it is stated that a similar pathway for hydrogenation of maleic anhydride to tetrahydrofuran, gamma butyrolactone and butanediol and hydrogenation of gamma butyrolactone to pyrrolidones is valid for the conversion of itaconic acid to its derivatives.

A.3.11 Production of 3-Hydroxybutyrolactone and Its Derivatives

The conventional production of 3-hydroxybutyrolactone is from malic acid reduction. Production of derivatives from 3-hydroxybutyrolactone are not provided by the literature. Additionally, except 3-Hydroxytetrahydrofuran production from catalytic dehydration of butane 1,2,4-triol [51], commercial production routes for its derivatives are not reported in the literature.

A.3.12 Production of Xylitol and Its Derivatives

Xylitol and arabinitol are produced from hydrogenation of their corresponding sugars xylose and arabinose. Production of xylitol is costly due to high price of xylose [1]. Production routes of xylaric acid, propylene and ethylene glycols are provided by the literature.

Table A.6 Production of Xylitol Derivatives

Derivative	Bio-based Production Route
Xylaric Acid	• Selective oxidation of xylitol[1]
Propylene Glycol	• Hydrogenolysis of xylitol[1]
Ethylene Glycol	• Hydrogenolysis of xylitol[1]

A.4 Commercial Production Routes of Products

Commercial production of acrylamide, acrylonitrile, acrylic acid, 2-methyl-1,4 butanediol, ethylene glycol, gamma-butyrolactone (GBL), glutaric acid, malonic acid, N-methyl pyrrolidone (NMP), 3-hydroxytetrahydrofuran, 1,5 pentanediol, 1,3 propanediol and propylene glycol are reported the literature.

Table A.7 Commercial Production Routes of Acrylamide, Acrylonitrile, Acrylic Acid, 2-Methyl-1,4 Butanediol, Ethylene Glycol, GBL, Glutaric Acid, Malonic Acid, NMP, 3 -Hydroxytetrahydrofuran, 1,5 Pentanediol, 1,3 Propanediol, Propylene Glycol

Derivative	Commercial Production Route
Acrylamide	Hydrogenation of acrylonitrile [52]
Acrylic Acid	• Oxidation of acrolein [53] • Carbonylation of acetylene [31&54] • Hydrolysis of acrylonitrile [31&54] • Reaction of ketene and formaldehyde [29] • Oxidation of propylene[54] • Dehydration of lactic acid [55]
1,4 Butanediol	• Reppe process- reaction of acetylene with formaldehyde [58&59] • Oxidative acetoxylation of 1, 3 butadiene [29] • ARCO process- Hydroformylation of allyl alcohol [58] • Reaction of propylene and acetic acid [29] • Direct hydrogenation of maleic anhydride[58]

Table A.7 (cont'd) Commercial Production Routes of Acrylamide, Acrylonitrile, Acrylic Acid, 2-Methyl-1,4 Butanediol, Ethylene Glycol, GBL, Glutaric Acid, Malonic Acid, NMP, 3 -Hydroxytetrahydrofuran, 1,5 Pentanediol, 1,3 Propanediol, Propylene Glycol

Ethylene Glycol	• Hydrogenation of ethylene oxide [59] • Oxidation of ethylene [29]
Acrylonitrile	• Ammoxidation of propylene [56&57] • Cyanation or oxidation of ethylene [29]
Gamma Butyrolactone	• Dehydrogenation of gamma-butyric acid [60] • Oxidation of tetrahydrofuran [60] • Hydrogenation of succinic or maleic acid anhydride [60&61]
Glutaric Acid	• Reaction of trimethylene cyanide with hydrochloric acid [62] • Reaction of GBL with KCN and HCl in aqueous media [63]
3-Hydroxytetrahydrofuran	• Catalytic dehydration of butane 1,2,4 triol [51]
Malonic Acid	• Hydrolysis of cyanoacetic acid with hydrochloric acid [64]
NMP	• Reaction of GBL with methyl amine [45]
1,5 Pentanediol	• Hydrolysis of tetrahydrofurfuryl alcohol [63]
1,3 Propanediol	• Hydration of acrolein [24] • Hydroformylation of ethylene oxide [25]
Propylene Glycol	• Hydrolysis of propylene [37] • Hydrogenation of dihydroxyacetone [37] • Catalytic hydrogenation of lactic acid [37]

APPENDIX B

DESCRIPTION OF SMILES NOTATION & BCFWIN

B.1 Description of SMILES Notation [12]

Simplified Molecular Input Line Entry System (SMILES) notation represents molecular structures as two - dimensional picture of the molecules drawn on a paper. It encodes the molecules and serves as a chemical language.

SMILES notations compose of **atoms** (designated by atomic symbols), **bonds**, parentheses (for **branching**), and numbers (designate **ring opening and closing positions**). With the exception of designating ring positions, numbers are not used in SMILES notation.

Atoms represented by their atomic symbols. For instance:

- C is carbon
- N is nitrogen
- S is sulfur
- O is oxygen

Upper and lower case letters are important. All aliphatic atoms in the structures are written in the upper case; whereas aromatic ones are entered in lower case letters. Current estimation method uses only carbon, nitrogen, oxygen, sulfur and selenium atoms. With the exception of hydrogen attached to aliphatic or aromatic nitrogen with a valence more than +3, hydrogen is not entered by the user. Software directly completes the required hydrogen atoms.

For example:

Chemical Name	Molecular Formula	SMILES Notation
Propane	CH3-CH2-CH3	CCC
Bromoethane	CH3-CH2-Br	CCBr
Ethanol	CH3-CH2-OH	CCO
Propylamine	CH3-CH2-CH2-NH2	CCCN

More examples of the SMILES notation are available on the SMILES example page [12].

Bonds are classified as: single bond, double bond, triple bond and aromatic bond. Single bonds are not shown and usually omitted. Unlike single bond, double and triple bonds should be designated by the symbols. Double bond is represented by the equality symbol "=" and triple bond is shown by the number symbol "#". Aromatic bond has no designation. It is shown by "lower case letter" and numbers are used to indicate the ring opening and closing positions. Examples of the designations are as follows:

Chemical Name	Molecular Formula	SMILES Notation
Ethylene	CH2=CH2	C=C
Propylene	CH2=CH-CH3	C=CC
2-Butene	CH3-CH=CH-CH3	CC=CC
Acetylene	H–C ≡ C-H	C#C
Acrylonitrile	CH2=CC≡N	C=CC#N
Benzene		c1ccccc1

Branches are shown by parentheses. The important point for branches is that SMILES notation of the molecule can not begin with the parentheses. For example,

(C) CCO is an invalid SMILES notation. Also, if an atom has more than one branch, branches are coded as consecutive pairs of parentheses. If the branch is connected to the carbon with double or triple bonds, this carbon atom, bond symbol and the connected carbon should be included in the parentheses. For instance, C = (CC)C is incorrect, it should be designated as C(=CC)C.

Lastly, SMILES notation of a molecule can be interpreted in different forms. The following example illustrates both the branching and the use of different but correct and acceptable notations of isobutyric acid:

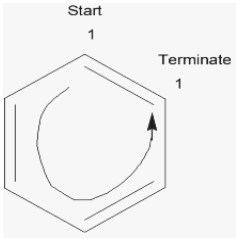
Molecular Structure	**SMILES Notation**
CH_3 OH | | CH –C =O | CH_3	CC(C)C(=O)O C(C)(C)C(=O)O OC(=O)C(C)C O=C(O)C(C)C

Isobutyric acid

The rules applied to write cyclic structures are:

- Cyclic structures necessitate numbers in order to indicate the starting and terminating atom of the ring.
- The number indicating starting and terminating atom should be same to show that these atoms are connected to each other.
- Numbers are entered immediately from the atoms to show the starting and terminating positions.
- Each number that is used must appear twice in the entire SMILES notation.
- If one starting or terminating atom is connected to other numbered atom then, the atom can be followed with two consecutive numbers.

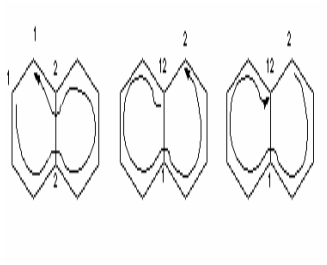
Following examples indicate the use of these encoding rules. The first example indicates the benzene structure and its SMILES notation and the second example shows the structure of naphthalene and different notations of naphthalene.



SMILES Notation

c1ccccc1

Figure B.1 Molecular Structure and SMILES Notation of Benzene



SMILES Notations

c1ccc2ccccc2c1

c12ccccc1cccc2

c2cccc1ccccc12

Figure B.2 Molecular Structure and SMILES Notations of Naphthalene

B.2 Description of Bioconcentration Factor Estimation Program (BCFWIN)

BCFWIN estimates the bioconcentration factor (BCF) of an organic compound using the compound's log octanol-water partition coefficient (Kow). Estimation methodology of the program includes the classification of a compound as either ionic or non-ionic. Ionic compounds include carboxylic acids, sulfonic acids and salts of sulfonic acids, and charged nitrogen compounds (nitrogen with a +5 valence such as quaternary ammonium compounds). All other compounds are classified as non-ionic [12].

Non-ionic compounds are predicted by the following relationships:

- $\log BCF = 0.77 \log Kow - 0.70 + \text{Sum } F(i)$ (log Kow 1.0 to 7.0) (B.1)
- $\log BCF = -1.37 \log Kow + 14.4 + \text{Sum } F(i)$ (log Kow > 7.0) (B.2)
- $\log BCF = 0.50$ (log Kow < 1.0) (B.3)

where Sum F(i) is the summation of structural correction factors

Ionic compounds are predicted as follows:

- $\log BCF = 0.50$ (log Kow < 5.0) (B.4)
- $\log BCF = 0.75$ (log Kow 5.0 to 6.0) (B.5)
- $\log BCF = 1.75$ (log Kow 6.0 to 7.0) (B.6)
- $\log BCF = 1.00$ (log Kow 7.0 to 9.0) (B.7)
- $\log BCF = 0.50$ (log Kow > 9.0) (B.8)

APPENDIX C

SAMPLE CALCULATION FOR ATOM AND MASS EFFICIENCY OF ETHYLENE GLYCOL PRODUCTION ROUTES

Atom and mass efficiency results of ethylene glycol production routes are presented in Table 4.33 in RESULTS AND DISCUSSION.

C.1 Atom and Mass Efficiency Calculations for Hydrolysis of Ethylene Oxide Route

$$C_2H_4O + H_2O \rightarrow HOCH_2CH_2OH \quad \text{(C.1)}$$

Atom efficiency: $\dfrac{NumberOfAtoms\,\mathrm{Pr}esentInThe\,\mathrm{Pr}oduct}{NumberOfAtoms\,\mathrm{Pr}esentInTheRawMaterials}$ (C.2)

Carbon efficiency: 100 %, Hydrogen efficiency: 100 %, Oxygen efficiency: 100 %

Mass efficiency: $\dfrac{TheMassOfThe\,\mathrm{Pr}oduct}{TheMassOfTheRawMaterials}$ (C.3)

Mass efficiency: $\dfrac{62g/moleEthyleneGlycol}{44g/moleEthyleneOxide + 18g/moleWater}$: 100%

C.2 Atom and Mass Efficiency Calculations for Hydrogenolysis of Glycerol Route

$$C_3H_8O_3 \rightarrow HOCH_2CH_2OH + CH_3OH \quad \text{(C.4)}$$

Atom efficiency:

Carbon efficiency: 67 %, Hydrogen efficiency: 75 %, Oxygen efficiency: 67 %

Mass efficiency: $\dfrac{62g/moleEthyleneGlycol}{92g/moleGlycerol}$: 67%

APPENDIX D

JOBACK METHOD FOR THE ESTIMATION OF GIBBS FREE ENERGY, ENTHALPY OF FORMATION AND HEAT CAPACTIY VALUES [36]

The prediction equation for Gibbs free energy of formation is:

$$\Delta G_f^0(298K) = 53.88 + \sum \nu_j^{(i)} \Delta G_j \text{ (kJ / mole) [36]} \tag{D.1}$$

, where ν_j the number of the each group included in the structure and ΔG_j is the specific group contribution of each group to free energy change for the reaction.

The prediction equations for enthalpy of formation and heat capacity estimations are:

$$\Delta H_f^0(298K) = 68.29 + \sum_j \nu_j^{(i)} \Delta_{Hj} \text{ (kJ / mole)} \tag{D.2}$$

$$c_{pi}^{\ 0} = \left(\sum_j \nu_j^{(i)} \Delta a_j - 37.93 \right) + \left(\sum_j \nu_j^{(i)} \Delta b_j + 0.210 \right) T + \left(\sum_j \nu_j^{(i)} \Delta c_j - 3.91 \times 10^{-4} \right) T^2 + \left(\sum_j \nu_j^{(i)} \Delta d_j + 2.06 \times 10^{-7} \right) T^3 \tag{D.3}$$

T in K and c_{pi}^0 in J/mol. K

In order to obtain more information on the group contributions for Gibbs free energy, enthalpy of formation and heat capacity estimations the cited reference can be used [36].

APPENDIX E

ASSUMPTIONS ON GLYCEROL UTILIZATION METABOLISMS FOR 1,3 PROPANEDIOL PRODUCTION PROCESSES

E.1 1,3 Propanediol Production from Glycerol Utilizing *Klebsiella pneumoniae*

As can be seen from Figure E.1, glycerol utilization metabolism of *Klebsiella pneumoniae* produces succinic acid, lactic acid, formate, ethanol, acetic acid, 2,3 butanediol as the by-products in addition to the desired product 1,3 propanediol. The assumption for the reaction stoichiometry is based on the the highest yield for the propanediol production. The maximum yield for the utilization of glycerol is approximately 0.67 mol/ mol of glycerol and the highest propanediol yield is expected with acetic acid as the only by-product in addition to H_2, CO_2 and water. The overall conversion of glycerol is approximated by the following stoichiometric equation [38]:

$$3Glycerol \rightarrow 2PDO(1,3) + CH_3COOH + CO_2 + H_2 + H_2O \qquad \text{(E.1)}$$

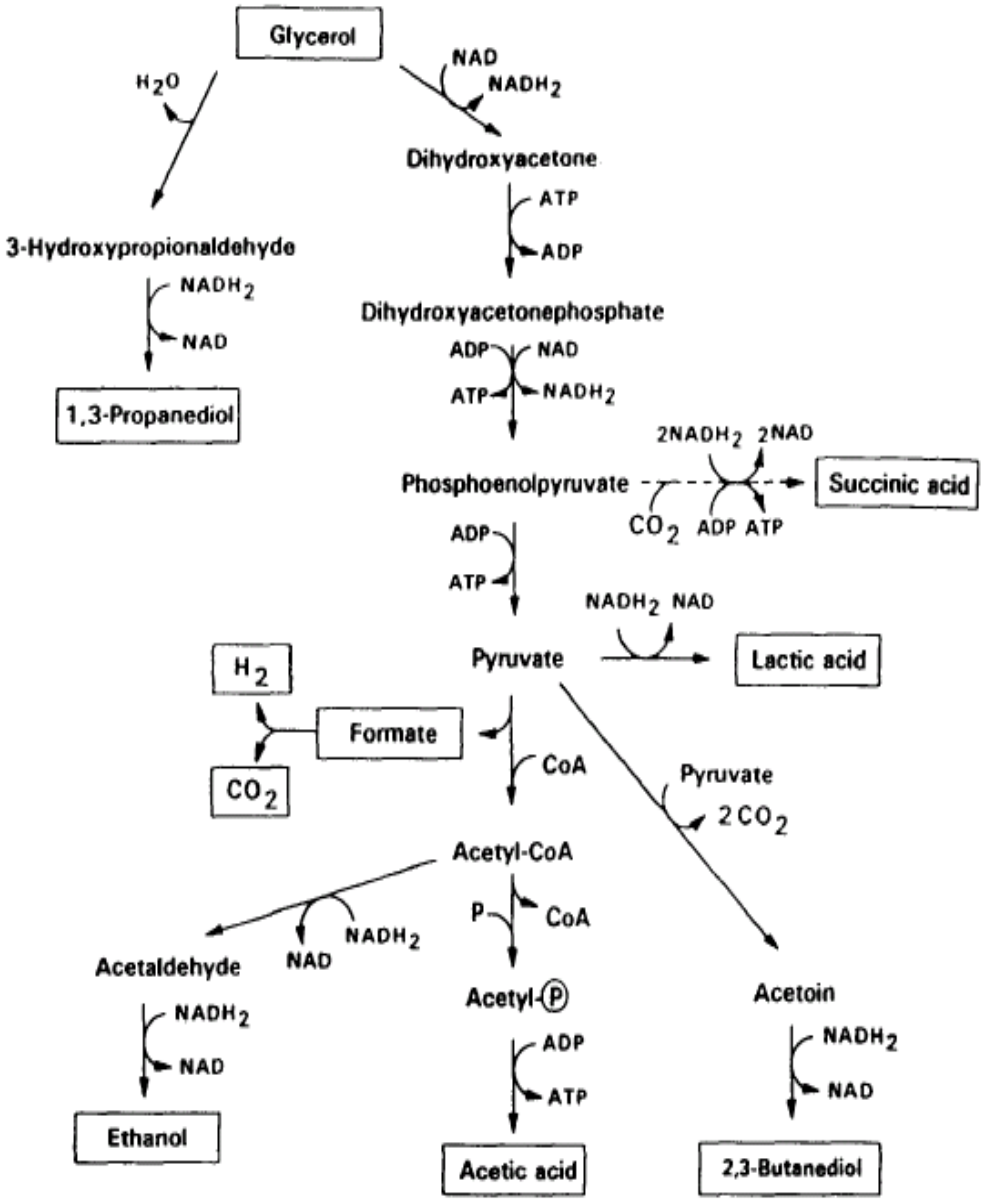


Figure E.1 The Anaerobic Glycerol Utilization Metabolism in *Klebsiella pneumoniae* [38]

E.2 1,3 Propanediol Production from Glycerol Utilizing Clostridium *butyricum*

Glycerol utilization mechanism for *Clostridium butyricum* is shown in Figure E.2. It can be seen from Figure E.2 that lactate, ethanol, acetate, butyrate, hydrogen and carbon dioxide are the by-products of glycerol utilization. However, laboratory scale experiments show that acetate and butyrate are found as the by-products [26]. Additionally, butyrate concentration is usually considerably higher than acetate concentration. If the butyrate is the only by product, then the yield of 1,3 propanediol is the highest. Therefore, considering the yield values provided by the literature given in Table E.1 and the reaction metabolism with this assumption, the reaction equation is approximated as:

$$6Glycerol \rightarrow 4PDO(1,3) + C_4H_8O_2 + 2CO_2 + 4H_2O \qquad \text{(E.2)}$$

Table E.1 Steady-State Yield Coefficients during Anaerobic Single-Stage Continuous Fermentation of Industrial Glycerol with *Clostridium butyricum* [26]

D (h^{-1})	$Y_{X/S}$ ($g\ g^{-1}$)	$Y_{PD/S}$ ($g\ g^{-1}$)	$Y_{But/S}$ ($g\ g^{-1}$)	$Y_{Ac/S}$ ($g\ g^{-1}$)
0.02	0.047	0.55	0.15	0.007

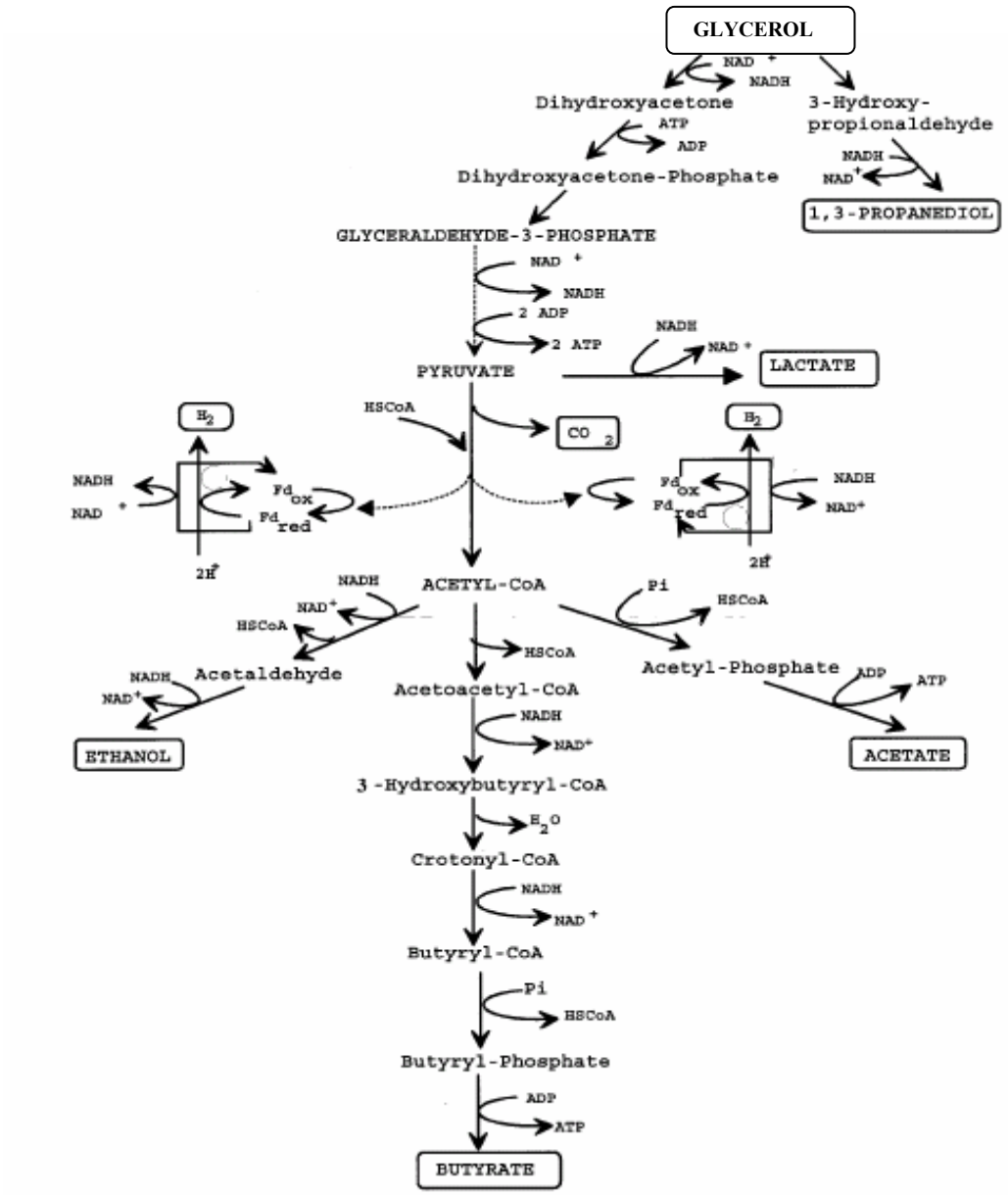


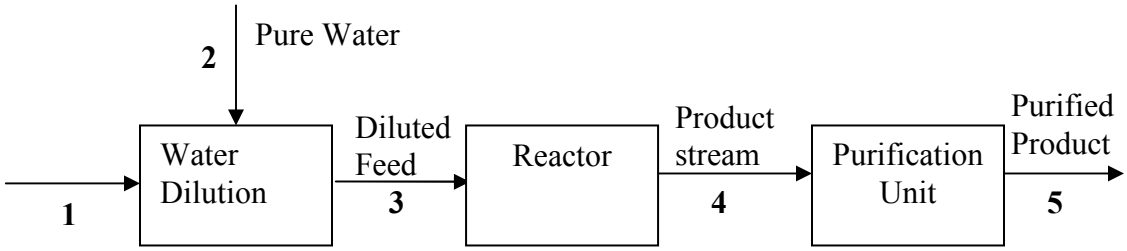
Figure E.2 Metabolic Pathway of Glycerol with *Clostridium butyricum* [26]

APPENDIX F

SAMPLE CALCULATIONS FOR 1,3 PROPANEDIOL PRODUCTION PROCESSES

F.1 Block Diagram Representation & Sample Calculations of 1,3 Propanediol Production from Glycerol Utilizing *Klebsiella pneumoniae* DSM 2026

Considering the features, design basis and reaction stoichiometry, a block diagram for the *Klebsiella pneumoniae* DSM 2026 process is drawn.



Stream 1: 70 wt % glycerol & 30 wt % water
Stream 3: 2.9 wt % glycerol & 97.1 wt % water
Stream 4: 1,3 propanediol, acetic acid, water, CO_2, H_2
Stream 5: 99.7 wt% 1,3 PDO & 0.03 wt % water

Figure F.1 Block Diagram Representation of 1,3 PDO Production with *Klebsiealla pneumoniae* DSM 2026

Table F.1 presents the inlet and outlet stream compositions for the reactor.

Table F.1 Inlet-Outlet Stream Composition and Enthalpy Values for 1,3 PDO Production with *Klebsiella pneumoniae* DSM 2026

Component	N in (mole/s)	H in (kJ/mole)	N out (mole/s)	H out (kJ/mole)
Glycerol	6.92	H_1	-	-
1,3 PDO	-	-	4.6	H_3
Acetic acid	-	-	2.3	H_4
CO_2	-	-	2.3	H_5
H_2O	1185	H_2	1187.3	H_6
H_2	-	-	2.3	H_7

In the above table, in order to obtain the enthalpy values and perform further calculations, the reference state selection should be made. Reference state is selected as: H_2O (l), CO_2 (g), PDO (l), glycerol (l), acetic acid (l) and H_2 (g) at 25 ˚C & 1 atm. Then, enthalpy values for H1-H7 are calculated for the desired temperatures. For glycerol and 1,3 propanediol, enthalpy of formation and heat capacity values are estimated using group contribution method. For the remaining chemicals the corresponding values are reported in the literature [39 & 68].

Table F.2 Enthalpy of Formation and Heat Capacity Values for the Raw Materials and Products

Component	**Enthalpy of formation (kJ/mole)**	**Heat capacity values**				**Unit**
		a	**b**	**c**	**d**	
Glycerol	-567.22	14.352	-0.0113	-2.338 $x10^{-4}$	5.34 $x10^{-8}$	J/mole K
Acetic acid	-435.1	4.840	0.2549	-1.753 $x10^{-4}$	4.949 $x10^{-8}$	J/mole K

Table F.2 (cont'd) Enthalpy of Formation and Heat Capacity Values for the Raw Materials and Products

1,3 PDO	-409.71	10.743	0.1927	-2.002 $x10^{-4}$	4.41 $x10^{-8}$	J/mole K
CO_2	-393.5	36.11 $x10^{-3}$	4.233 $x10^{-5}$	-2.887 $x10^{-8}$	7.464 $x10^{-12}$	kJ/mole C
H_2O	-285.84 (l)	33.46 $x10^{-3}$	0.6880 $x10^{-5}$	0.7604 $x10^{-8}$	-3.593 $x10^{-12}$	kJ/mole C
H_2	0	28.84 $x10^{-3}$	0.00765 $x10^{-5}$	0.3288 $x10^{-8}$	0.869 $x10^{-12}$	kJ/mole C

In Table F.2, it is important to note that heat capacity value of water is valid for water vapor. Hence, calculations for liquid water are performed considering both heat capacity and heat of formation values of water vapor together with heat of formation value of liquid water. Using Table F.2 and the inlet and outlet stream temperatures, enthalpy values are calculated as follows:

Table F.3 Inlet and Outlet Stream Enthalpy Values for *Klebsiella pneumoniae* Process

Inlet-Outlet Stream Enthalpies	Enthalpy Values
H_1	-567.22 kJ/mole
H_2	-285.44 kJ/mole
H_3	- 409.085 kJ/mole
H_4	-434.29 kJ/mole
H_5	-393.05 kJ/mole

Table F.3 (cont'd) Inlet and Outlet Stream Enthalpy Values for *Klebsiella pneumoniae* Process

H_6	-285.17 kJ/mole
H_7	0.346 kJ/mole

Using inlet & outlet stream compositions and enthalpy values, energy balance is performed.

$Q = \Delta H$ and $\Delta H = \sum n_{out} H_{out} - \sum n_{in} H_{in}$

$$\Delta H = \begin{array}{l} 4.6 molesofPDO \times \dfrac{-409.085kJ}{molePDO} + 1187.3 molesofH_2O \times \dfrac{-285.17kJ}{moleH_2O} + \\ 2.3 molesofAceticAcid \times \dfrac{-434.29kJ}{moleAA} + 2.3 molesofCO_2 \times \dfrac{-393.05kJ}{moleCO_2} \\ +2.3 molesofH_2 \times \dfrac{0.346kJ}{moleH_2} - 6.9 molesofGlycerol \times \dfrac{-567.22kJ}{moleGlycerol} \\ -1185 molesofH_2O \times \dfrac{-285.44kJ}{moleH_2O} \end{array}$$

$\Delta H =$ **-206 kJ /s**

Cooling water requirement of the reactor to keep the reaction temperature constant is calculated as:

$-\Delta H = m_{CW} \times Cp_{CW} \times \Delta T$; where Cp_{CW} : 4.1815 kJ/kg K and ΔT : 10 K

- m_{CW} : 25.09 kg/s and annually m_{CW} **: 4.93 kg / kg PDO.**
- The cost of cooling water: \$ 0.22 x 10^{-3} / kg PDO.
- The electricity demand : 0.004 kWh/ kg of 1,3 propanediol

Using Equation 3.8 and Table 3.14, emissions due to cooling water use are calculated and presented in Table F.4.

Table F.4 Emissions of SO_2, CO_2 and NO_X due to Electricity Use for Pumping of Cooling Water

SO_2 (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
1.2×10^{-9}	2.6×10^{-10}	2.2×10^{-9}

After reactor operations are completed, product stream enters to a purification unit, where 1,3 propanediol is purified to 99.7 wt % propanediol and 0.03 wt % water. The boiling point of 1,3 propanediol at 1 atm pressure is 514.15 K[40]. It is assumed that all acetic acid and most of the water should be removed. The heat of vaporization and boiling point data for acetic acid and water are presented in Table F.5.

Table F.5 Heat of Vaporization and Boiling Point Data for Acetic Acid and Water

Chemical	Heat of Vaporization (kJ/mole)	Boiling point (K)
Acetic acid	24.39 kJ/mole	391.35
Water	40.656 kJ/mole	373.15

Table F.6 Heat Requirements for Acetic Acid and Water Removal from the Product Stream

Chemical	Number of moles that is removed	Heat requirement
Acetic acid	2.3 moles/s	30.37 kJ/mole
Water	1186.94 moles/s	43.64 kJ/mole

Heat requirement for the final purification operation is calculated as 51,868 kJ/s.

- Steam Usage:

$$\dot{m}_{steam} = \frac{\Delta H_{req}}{\hat{H}_{steam}} = \frac{51{,}868 kJ/s}{2764.15 kJ/kg} = 18.76 \text{ kg /s.}$$

- Amount of steam used per kg of 1,3 propanediol: 53.67 kg steam/kg of 1,3 propanediol
- The cost of steam is: $ 0.32 /kg of 1,3 propanediol

Emissions of the gases due to natural-gas combustion are given in Table F.7.

Table F.7 Emissions of SO_2, CO, CO_2 and NO_X for Natural Gas Combustion to Purify the Reactor Outlet Stream

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.5×10^{-2}	6.35	8.98×10^{3}	1.06×10^{1}

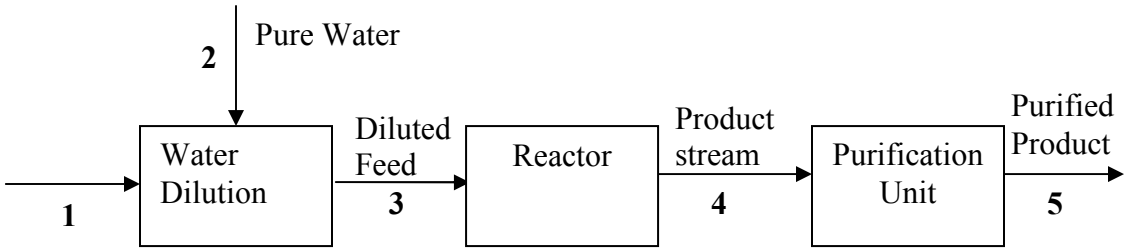
The results of the releases due to secondary emissions are summarized in Table F.8.

Table F.8 Emissions of SO_2, CO, CO_2 and NO_X due to Utility Usage During 1,3 Propanediol Production with *Klebsiella pneumoniae* DSM 2026

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.5×10^{-2}	6.35	8.98×10^{3}	1.06×10^{1}

F.2 Block Diagram Representation and Sample Calculations of 1,3 Propanediol Production from Glycerol Utilizing *Clostridium butyricum* F2b

The block diagram representation of 1,3 propanediol from *Clostridium butyricum* F2b process is presented in Figure F.2.



Stream 1: 70 wt % glycerol & 30 wt % water
Stream 3: 2.9 wt % glycerol & 97.1 wt % water
Stream 4: 1,3 propanediol, butyric acid, water, CO_2
Stream 5: 99.7 wt% 1,3 PDO & 0.03 wt % water

Figure F.2 Block Diagram Representation of 1,3 PDO Production with *Clostridium butyricum* F2b

Table F.9 presents the inlet and outlet stream compositions for the reactor.

Table F.9 Inlet-Outlet Stream Compositions for the Reactor Operation

Component	N in (mole/s)	H in (kJ/mole)	N out (mole/s)	H out (kJ/mole)
Glycerol	6.9	H_1	-	-
1,3 PDO	-	-	4.6	H_3
Butyric acid	-	-	1.15	H_4
CO_2	-	-	2.3	H_5
H_2O	1184.7	H_2	1189.3	H_6

Reference state is selected as the one given in the first process. Enthalpy values of formation and heat capacity values for the reactants and products are given in Table F.10 [36]. Enthalpy values of the streams are calculated using Table F.10 and presented in Table F.11.

Table F.10 Enthalpy of Formation and Heat Capacity Values for the Raw Materials and Products

Component	**Enthalpy of formation (kJ/mole)**	**Heat capacity values**				**Unit**
		a	**b**	**c**	**d**	
Glycerol	-567.22	14.352	-0.0113	-2.338 $x10^{-4}$	5.34 $x10^{-8}$	J/mole K
Butyric acid	-476.16	3.852	0.4356	-2.664 $x10^{-4}$	6.44 $x10^{-8}$	J/mole K
1,3 PDO	-409.71	10.743	0.1927	-2.002 $x\ 10^{-4}$	4.41 $x\ 10^{-8}$	J/mole K
CO_2	-393.5	36.11 $x10^{-3}$	4.233 $x10^{-5}$	-2.887 $x10^{-8}$	7.464 $x10^{-12}$	kJ/mole C
H_2O	-285.84 (l)	33.46 $x10^{-3}$	0.6880 $x10^{-5}$	0.7604 $x10^{-8}$	-3.593 $x10^{-12}$	kJ/mole C

Table F.11 Inlet and Outlet Stream Enthalpy Values for *Clostridium butyricum* Process

Inlet-Outlet Stream Enthalpies	Enthalpy Values
H_1	-567.22 kJ/mole
H_2	-285.44 kJ/mole
H_3	-409.29 kJ/mole
H_4	-475.26 kJ/mole

Table F.11 (cont'd) Inlet and Outlet Stream Enthalpy Values for *Clostridium butyricum* Process

H_5	-393.21 kJ/mole
H_6	-285.11 kJ/mole

The inlet & outlet stream compositions and enthalpy values are used in the energy balance:

$Q = \Delta H$ and $\Delta H = \sum n_{out} H_{out} - \sum n_{in} H_{in}$

$$\Delta H = \begin{aligned} & 1189.3 molesofH_2O \times \frac{-285.18kJ}{moleH_2O} + 4.6 molesofPDO \times \frac{-409.29kJ}{molePDO} + \\ & 1.15 molesofButyricAcid \times \frac{-475.26kJ}{moleBA} + 2.3 molesofCO_2 \times \frac{-393.21kJ}{moleCO_2} \\ & -6.9 molesofGlycerol \times \frac{-567.22kJ}{moleGlycerol} - 1184.7 molesofH_2O \times \frac{-285.44kJ}{moleH_2O} \end{aligned}$$

$\Delta H =$ **-471.04 kJ/s**

Cooling water requirement of the reactor to keep the reaction temperature constant is calculated as:

$-\Delta H = m_{CW} \times Cp_{CW} \times \Delta T$; where Cp_{CW} : 4.1815 kJ/kg K and ΔT : 10 K

- m_{CW} : 11.26 kg/s and **32.22 kg / kg PDO.**
- The cost of cooling water: \$ 1.45 x 10^{-3} / kg PDO
- The electricity demand: 0.02 kWh/ kg of 1,3 propanediol

Emissions associated with the use of electricity are presented in Table F.12.

Table F.12 Emissions of SO_2, CO_2 and NO_X Due to Electricity Use for Pumping of Cooling Water

SO_2 (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
1.32×10^{-9}	1.12×10^{-10}	5.79×10^{-11}

After reactor operations are completed, product stream enters to a purification unit, where 1,3 propanediol is purified to 99.7 wt % propanediol and 0.03 wt % water. Boiling point of 1,3 propanediol is 514.15 K [40]. It is assumed that all butyric acid and most of the water should be removed. The boiling point of butyric acid is 436.55 K and its heat of evaporation is 43.79 kJ/mole. Heat requirements for butyric acid and water removal are presented in Table F.13.

Table F.13 Heat Requirements for Butyric Acid and Water Removal from the Product Stream

Compound	Number of moles that is removed	Heat requirement
Butyric acid	1.15 moles/s	60.93 kJ/mole
Water	1189.3 moles/s	42.47 kJ/mole

Total heat requirement for purification unit is calculated as 50,579 kJ/s. Heat is supplied with steam having the same properties as described in the first process.

- Steam Usage:

$$\dot{m}_{steam} = \frac{\Delta H_{req}}{\hat{H}_{steam}} = \frac{50,579 kJ/s}{2764.15 kJ/kg} = 18.30 \text{ kg /s.}$$

- Amount of steam used per kg of 1,3 propanediol: 52.34 kg steam/kg of 1,3 propanediol
- The cost of steam is: $ 0.31 /kg of 1,3 propanediol

Emissions of the gases due to natural-gas combustion are given in Table F.14.

Table F.14 Emissions of SO_2, CO, CO_2 and NO_X Due to Natural Gas Combustion to Supply the Energy Needed for Purification of Product Stream

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.4×10^{-2}	6.18	8.73×10^{3}	1.03×10^{1}

The results of the releases due to secondary emissions are summarized in Table F.15.

Table F.15 Emissions of SO_2, CO, CO_2 and NO_X due to Utility Usage in 1,3 Propanediol Production with *Clostridium butyricum*

SO_2 (kg/kg 1,3 PDO)	CO (kg/kg 1,3 PDO)	CO_2 (kg/kg 1,3 PDO)	NO_X (kg/kg 1,3 PDO)
4.4×10^{-2}	6.18	8.73×10^{3}	1.03×10^{1}

APPENDIX G

TABLES FOR DEGRADATION HALF-LIVES OF DERIVATIVES

Table G.1 Degradation Half-life Values of Glycerol Derivatives in Air, Water, Soil and Sediment

Glycerol Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
Glyceric Acid	1.5	8.7	17	78
Glycerol Carbonate	1.9	15	30	135
Diglyceraldehyde	0.37	8.7	17	78
Propanol	2.9	15	30	135
Propylene Glycol	1.3	8.7	17	78
1,3 Propanediol	1.7	8.7	17	78
Glycidol	3.5	15	30	135

Table G.2 Degradation Half-life Values of Aspartic Acid Derivatives in Air, Water, Soil and Sediment

Aspartic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
2 Amino 1,4 BDO	0.27	8.7	17	78
3 amino THF	0.2	15	30	135
Amino-2-Pyrrolidone	0.14	15	30	135

Table G.2 (cont'd) Degradation Half-life Values of Aspartic Acid Derivatives in Air, Water, Soil and Sediment

Aspartic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
AminoGBL	0.25	15	30	135
Aspartic Anhydride	0.62	15	30	135

Table G.3 Degradation Half-life Values of 3-Hydroxypropionic Acid Derivatives in Air, Water, Soil and Sediment

3-HPA Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
Acrylic Acid	1.3	8.7	17	78
Acrylamide	1.2	15	30	135
Acrylonitrile	3.8	15	30	135
Ethyl-3HP	2.6	15	30	135
Malonic Acid	10	8.7	17	78
Methyl Acrylate	1.5	15	30	135
1,3 Propanediol	1.7	8.7	17	78
Propiolactone	26	15	30	135

Table G.4 Degradation Half-life Values of Glucaric Acid Derivatives in Air, Water, Soil and Sediment

Glucaric Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
Alpha keto glucarates	0.35	2.3	4.7	21
Glucarodilactone	2.2	8.7	17	78
Glucaro gamma lactone	0.39	8.7	17	78
Glucaro sigma lactone	0.58	2.3	4.7	21

Table G.5 Degradation Half-life Values of Itaconic Acid Derivatives in Air, Water, Soil and Sediment

Itaconic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
2 methyl 1,4 BDO	1.2	8.7	17	78
2 methyl 1,4 BDA	0.24	15	30	135
3 methyl THF	0.96	15	30	135
3-4 methyl NMP	0.62	15	30	135
3-4 methyl GBL	4.6	15	30	135
3 Methyl Pyrolidone	0.2	15	30	135
Itaconic Diamide	0.42	15	30	135

Table G.6 Degradation Half-life Values of Levulinic Acid Derivatives in Air, Water, Soil and Sediment

Levulinic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
1,4 pentanediol	1.3	8.7	17	78
2 methyl THF	0.75	15	30	135
Acrylic Acid	1.3	8.7	17	78
B-Acetyl Acrylic Acid	0.75	8.7	17	78
D-Aminolevulinate	0.5	8.7	17	78
G-Valerolactone	4.2	15	30	135
Angelilactones	0.54	15	30	135
Diphenolic Acid	0.19	15	30	135

Table G.7 Degradation Half-life Values of Glutamic Acid Derivatives in Air, Water, Soil and Sediment

Glutamic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
1,5 Pentandiol	1.3	8.7	17	78
5 Amino-1-Butanol	0.2	15	30	135
Glutaminol	0.27	8.7	17	78
Glutaric Acid	5.8	8.7	17	78
Norvoline	0.35	8.7	17	78
Proline	0.19	8.7	17	78
Prolinol	0.17	15	30	135
Pyroglutamic Acid	1.1	15	30	135
Pyroglutaminol	0.79	15	30	135

Table G.8 Degradation Half-life Values of Xylitol Derivatives in Air, Water, Soil and Sediment

Xylitol Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
Ethylene Glycol	2.1	8.7	17	78
Propylene Glycol	1.3	8.7	17	78
Glycerol	0.88	8.7	17	78
Lactic Acid	2.7	8.7	17	78
Xylaric Acid	0.67	2.3	4.7	21
Mixture of hydroxyl furans	0.46	8.7	17	78

Table G.9 Degradation Half-life Values of Sorbitol Derivatives in Air, Water, Soil and Sediment

Sorbitol Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
Ethylene Glycol	2.1	8.7	17	78
Propylene Glycol	1.3	8.7	17	78
Glycerol	0.88	8.7	17	78
1,4 Sorbitan	0.37	8.7	17	78
2,5 Anhydrosugars	0.36	8.7	17	78
Isosorbide	0.62	15	30	135
Lactic Acid	2.7	8.7	17	78

Table G.10 Degradation Half-life Values of Succinic Acid Derivatives in Air, Water, Soil and Sediment

Succinic Acid Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
1,4 Butanediol	1.5	8.7	17	78
1,4 Diaminobutane	0.24	15	30	135
2-Pyrrolidone	1.3	15	30	135
DBE	12	15	30	135
GBL	7.1	15	30	135
Succindiamide	1.7	15	30	135
Succinonitrile	380	15	30	135
NMP	1.3	15	30	135
THF	1	15	30	135

Table G.11 Degradation Half-life Values of 2,5 FDCA Derivatives in Air, Water, Soil and Sediment

2,5 FDCA derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
2,5 bisTHF	0.18	15	30	135
2,5 Dihydroxy Methylfuran	0.12	15	30	135
2,5 Furan Dicarbaldehyde	0.4	15	30	135
2,5 Dihydroxymethyl THF	0.5	15	30	135
Succinic Acid	5.8	8.7	17	78

Table G.12 Degradation Half-life Values of 3- Hydroxybutyrolactone Derivatives in Air, Water, Soil and Sediment

3-Hydroxybutyrolactone Derivatives	Degradation Half-life (days)			
	Air	Water	Soil	Sediment
2-Amino 3-Hydroxy THF	0.13	15	30	135
3- Amino THF	0.2	15	30	135
3 Hydroxy THF	0.88	15	30	135
Acrylate-Lactone	1	15	30	135
Epoxy-Lactone	11	15	30	135
G-Butenyl-Lactone	1.3	15	30	135

APPENDIX H

MARKET PRICE INFORMATION FOR PETROCHEMICALS

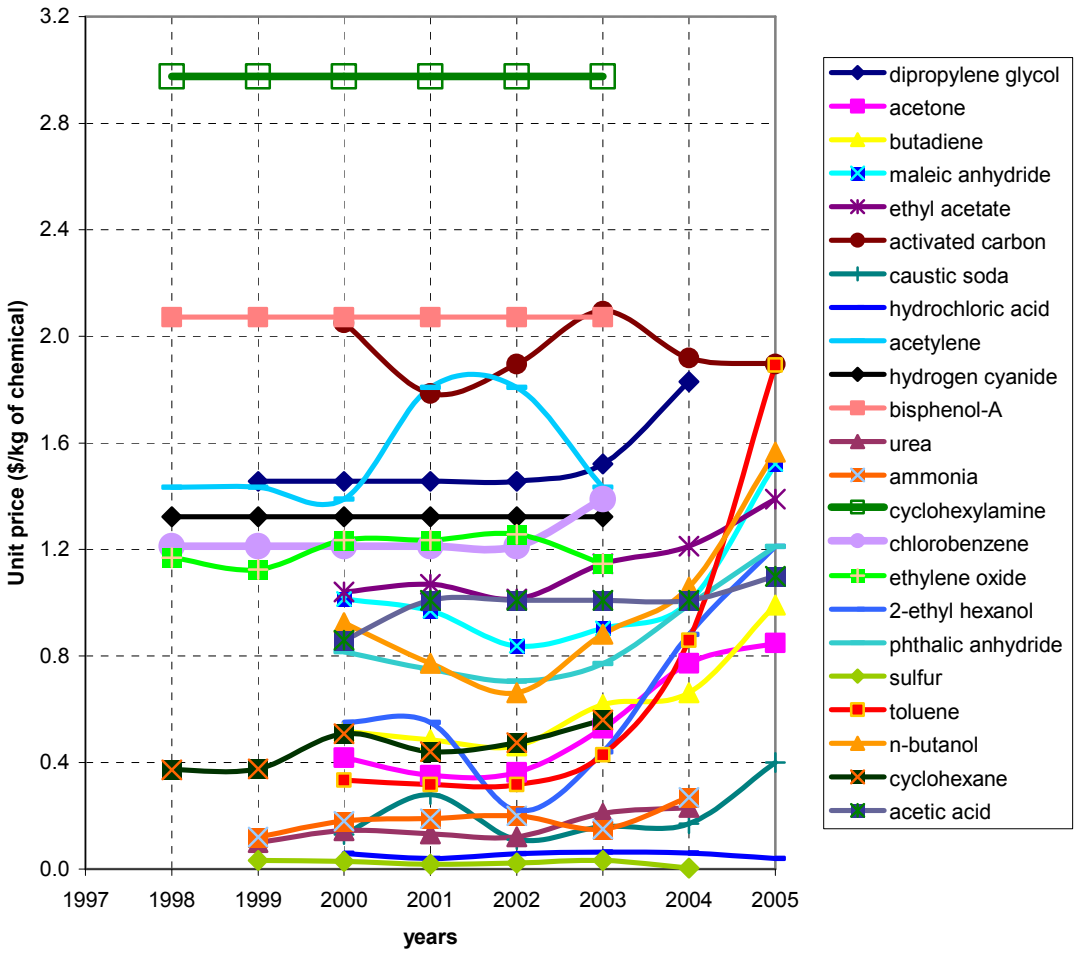


Figure H.1 Market Price Information for Petrochemicals Between the Years 1997 and 2005 [32]

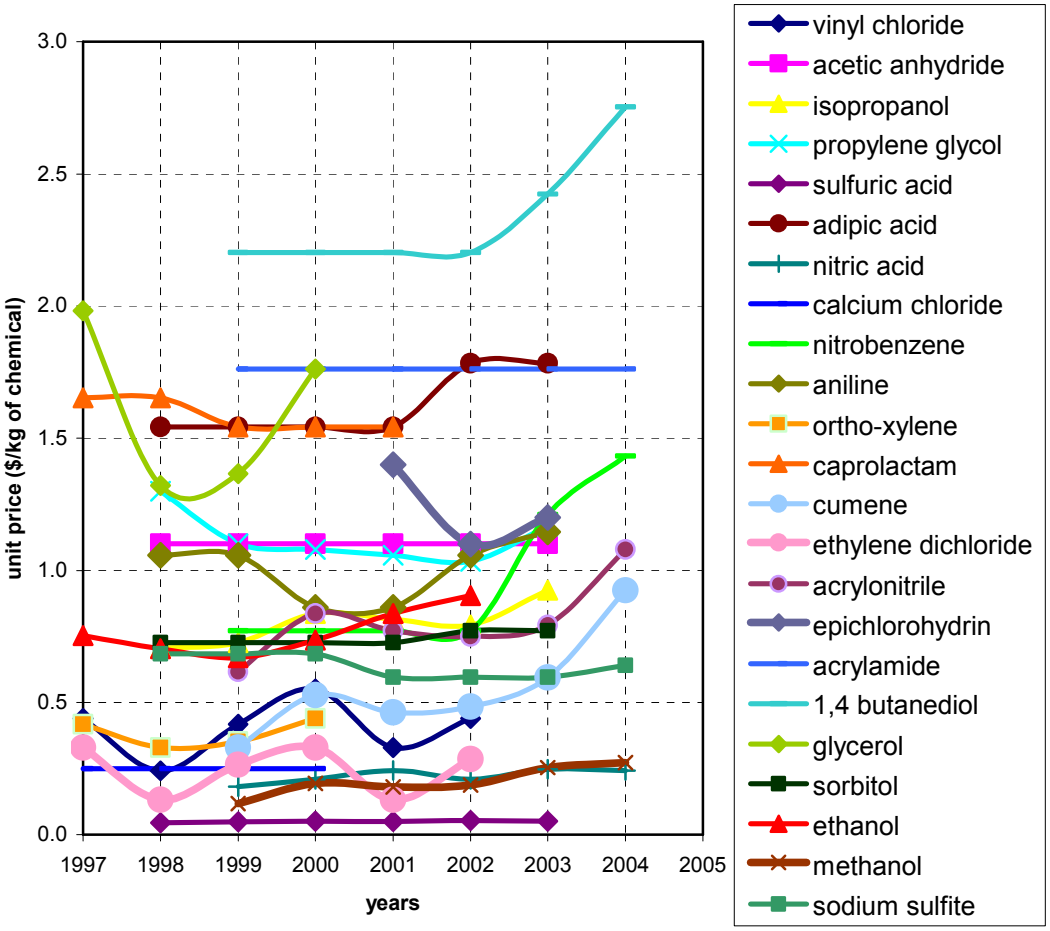


Figure H.1 (cont'd) Market Price Information for Petrochemicals Between the Years 1997 and 2005 [32]

Table H.1 Chemical Prices Selected for Economical Potential Calculations

Chemical	Selected price $ / kg of chemical	Chemical	Selected price $ / kg of chemical
Acetone	0.364	Ethylene glycol	1.101
Acetic acid	1.010	2-ethyl hexanol	0.220
Acetic anhydride	1.101	Ethylene oxide	1.257
Acetylene	1.808	Epichlorohydrin	1.100
Activated carbon	1.896	Formaldehyde	0.4
Acrylamide	1.762	Glycerol	1.700
Acrylic acid	1.455	Hydrochloric acid	0.058
Acrylonitrile	0.749	Hydrogen cyanide	1.323
Adipic acid	1.784	Isopropanol	0.793
Ammonia	0.200	Maleic anhydride	0.838
Aniline	1.057	Methanol	0.187
Bisphenol-A	2.072	n-butanol	0.661
Butadiene	0.463	Nitric acid	0.209
1,4 butanediol	2.203	Nitrobenzene	0.771
Calcium chloride	0.250	Orthoxylene	0.386
Caprolactam	1.542	Phthalic anhydride	0.705
Caustic soda	0.110	Propylene glycol	1.035
Chlorobenzene	1.213	Sodium sulfite	0.596
Cyclohexane	0.475	Sorbitol	0.771
Cyclohexylamine	2.976	Sulfur	0.023
Cumene	0.485	Sulfuric acid	0.053
Dipropylene Glycol	1.455	Toluene	0.318
Ethanol	0.904	Urea	0.121
Ethyl acetate	1.014	Vinyl Chloride	0.441
Ethylene dichloride	0.286		