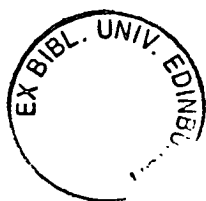# The Identification of Side Reactions and Byproducts in Process Synthesis
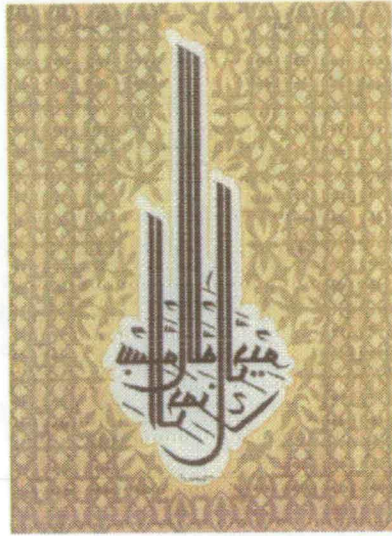
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PhD Thesis
Submitted as a requirement for the degree of
Doctor of Philosophy

School of Chemical Engineering
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Scotland, United Kingdom

September 1999

In the name of Allah, the Compassionate
the Most Merciful

Declaration

I hereby declare that the thesis is composed by me, and all work is done by me. All references to other people's work are appropriately cited.

Acknowledgment

Preface

This thesis is the compilation of the study on the automated identification of side reactions and byproducts. The present work emphasises organic chemical based industrial processes whose chemical properties can be detemined by using a group contribution technique. The procedures described in this thesis may help simplify computational representation of organic chemical structures and thus reactions. It is expected that the application of the programs to industrial processes would provide insight into the reactive behaviour of chemical reaction systems as well as the behaviour of byproducts in the recycle systems.

The materials selected for the case studies manifest the capability of the software. Comparisons with experiments demonstrate the applicability of the programs to generate reaction networks similar to that of the experiments. The application of the programs to side reaction generation in several chemical processes indicates that the programs are capable of identifying byproducts beside the major species that are already known and had been identified. Further investigation on the separability of these species has led to the determination of the species flow in the process line. With this, it is concluded that this work has reached its objective.

However, readers may find some incomplete fulfillment in this work, and therefore constructive criticisms and corrections are appreciated. I hope that this work can be extended and is useful to others, so that the software has the benefit and be applied widely.

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Abstract

This work presents a systematic approach to the identification of possible byproducts in process synthesis. The objective is to discover all possible reactions that might take place in a reaction system, in addition to already known main reactions. These side reactions may generate species in minor quantities which can be difficult to separate and therefore be carried into the recycle system. These species can thus remain in the process and accumulate.

A literature survey indicated that generic languages for chemical reactions have been developed recently by other workers. These have adopted the concepts of fundamental chemistry with the aim of identifying major chemical reactions. For the purpose of the present work, strict interpretation of chemistry was not considered necessary since the aim was to generate minor species which *might* be formed. The work covers aspects of molecular representation, reaction generation and thermodynamic evaluation for screening. Molecular properties are estimated using group contribution methods. Unlikely species are ruled out using both stoichiometric and thermodynamic tests.

The approach was first tested by comparison with experimental work, on the partial wet oxidation of p-coumaric acid and alkylation of toluene with ethanol. This showed favourable results. Process case studies were then undertaken including vinyl chloride monomer and the preparation of R-134a and R-22. These processes have been used to study the effect of byproduct built-up. The study involved separation simulation to investigate the separability of the components. This confirmed that many potential byproducts would be difficult to separate and might tend to accumulate in recycles.

The results show that the approach has promise for identifying possible side reactions, byproducts and the problems what they will cause in a continuous process. Thus in the long term the approach affects the possibility of reducing and eliminating pilot plant studies in moving from laboratories to full scale processes.

Nomenclature

a	polynomial coefficient of heat capacity
a_ϵ	ratio of coefficient matrix of chemical s to coefficient matrix of chemical s-1
A_i	a ratio of sums and products of rate coefficients
b	polynomial coefficient of heat capacity
b_ϵ	ratio of coefficient matrix of product p to coefficient matrix of chemical s-1
BE	bond electron connection matrix
c	polynomial coefficient of heat capacity
C_o	the difference of price vector of chemical s+1 to chemical s-1
C_1	the difference of price vector of chemical s to chemical s-1
C_p^o	heat capacity
CT	connection table
d	polynomial coefficient of heat capacity
e	the number of elements
EM	matrix of ensemble of molecule
G	free energy
ΔG	free energy changes
ΔG_r	free energy of reaction
ΔG^o	standard free energy changes
ΔG_f^o	free energy of formation
ΔG_{rT}^0	standard free energy of reaction
$\Delta G_+, T_+$	intersection point of free energy as a function of temperature and q
ΔH	enthalpy changes
ΔH^o	standard enthalpy changes
ΔH_f^o	enthalpy of formation
I	integration constant
k	the number of species
$k_{[..]}$	rate coefficients of respective molecules (in square brackets)
K_{eq}	equilibrium constant
L_p	pathways that produce metabolites
L_c	pathways that consume metabolites
L_r	metabolites as intermediates
L_n	non-participating metabolites
m	degree of freedom
$\mathbf{M}$	matrix M
n_A	the number of atoms
n_j	the number of groups of the jth type

p_i	the price of chemical i per mole of i
$\underline{p}$	vector of elements p_i
p	product chemical
P_c	critical pressure
q	a parameter indicating the amount of chemicals in moles
q_s	the amount of chemicals used as specified stoichiometric coefficient
q_s^*	common intersection of q_s and gross added value of a number of chemicals
r	rank of element matrix
r_a	rank of atomic matrix
r_e	rank of (e^*s) matrix
$r_{[..]}$	rate of disappearing of respective molecules (in square brackets)
R	gas constant in J/k.mol
R_μ^o	large radicals with carbon number exceeding four
R_β^o	small chain propagating radicals
R_1	alkyl
R	reaction matrix
R	feasible region
s	the number of species
ΔS	entropy changes
T	temperature in Kelvin
T_o	lower temperature bound
T	upper temperature bound
T_c	critical temperature
T_b	boiling temperature
T_{opr}	operating temperature in Kelvin
V	gross added value
V_o	locality dependency of gross added value
V_c	critical volume
$\underline{v}_a^T$	vector of stoichiometric coefficients

Greek Symbols

$\alpha_{s,p,s-1}$	thermodynamic constant of chemical s, chemical s-1 and chemical p
$\beta_{s,p,s-1}$	thermodynamic constant of chemical s, chemical s-1 and chemical p
$\Delta_{...}$	contribution of the jth atomic or molecular groups
Γ	acceptable bounds
ϵ	element matrix
ν	vector for stoichiometric coefficients for all chemicals

Subscripts

a	polynomial coefficient of heat capacity
b	polynomial coefficient of heat capacity
c	polynomial coefficient of heat capacity
d	polynomial coefficient of heat capacity
G	free energy
H	enthalpy
P	pressure
T	temperature
V	volume

Contents

Chapter 1

Introduction

1.1 Background

This thesis describes the development of tools for automated identification of side reactions in chemical process synthesis. Process synthesis deals ultimately with the invention of techniques to produce chemicals by transforming raw materials into desired products. Facilities to generate this transformation are formulated, developed and evaluated in as much detail as appropriate. Complex and iterative procedures must be carried out because decision making in design and synthesis of chemical processes involves highly interconnected systems. Specification and identification of process structure is established predominantly by a heuristic but systematic approach, since the formulation for rigorous mathematical procedures remains intractable despite the advancement in computing tools to solve such formulations. Siirola[1], pursuing conceptual design from industrial perspective states that such systematical approach may reduce e.g. energy cost by up to 50 % and net present cost up to 35 %.

1.1.1 Process Synthesis

Douglas and Stephanopoulos[2] established a framework in conceptual process design using hierarchical approach. The procedures are divided into 6 levels of decision making :

- *Level 0-* Input information

- *Level 1-* Number of simple plants and the process connectivity

- *Level 2-* Input-output structure of the simple plants

- *Level 3-* Recycle structure of the simple plants

- *Level 4-* Separation system of the simple plants

- *Level 5-* Energy integration

- *Level 6-* Evaluation of alternatives

Level 0 is the crucial initial stage where input information such as chemistry data, economic constraints, feedstock availability, product specification and environmental regulations is collected. Level 4 and 5 are related to energy integration and separation systems which have received more attention in most work worldwide. The area of reaction synthesis which can be viewed as the very first step of process invention has not been looked at extensively in the last fifteen years, although significant development on reaction mechanisms and synthesis tools have been found in recent publications[14, 15, 16, 17, 24, 32, 33]. It is the central problem of the industry to discover new clusters of reactions for manufacturing a wide variety of chemicals, both for product improvement and product invention. The exploration of reaction paths can thus be seen as a key to competitiveness in the process industries.

1.1.2   Reaction Path Synthesis

Reaction path synthesis involves techniques to establish sequences of chemical reactions to obtain desired products. It is an important stage in process synthesis since it provides input information for process flowsheets where major pieces of equipment are enumerated. In some cases, commercially important chemicals are manufactured by converting raw materials through several reaction steps. Although information on feasible reactions and their stoichiometry can be obtained from the patent literature, a chemical route consisting of the feasible reactions must be selected to transform available raw material into desired products[1, 5].

The synthesis of reaction paths can generate extremely large problems, so large scale computing resources would be required to implement an exhaustive search. However, software techniques based on object oriented concepts, knowledge based models and declarative reasoning can now provide a comprehensive approach to such complex problems.

The application of computer technology has provided methods for the automation of reaction path synthesis which is preceded by acquiring, storing and searching for information on chemical compounds. This has also influenced the development of chemical structure representation and currently led to the development of languages for chemical reactions.

1.1.3   Chemical Structure Representation

Early automation of chemical structure representation was developed mainly for organic chemists searching for new structural types. Unlike inorganic chemistry, reactions of organic chemistry are developed based on experimental work or previously developed procedures. Therefore, storing information became crucial and data files had to be able to hold complex structures. A suitable representation should serve the main purposes of retrieval of compounds, substructure classification and dealing with reaction mechanisms. Consequently, the essential features of the system must comprise the total description of molecules but be relatively easy and inexpensive to use[26, 27, 28].

The evolution of structural representation follows the development of computer technology. Nowadays, chemists can use graphic displays to interact with the machines. However, beneath the user friendly interactive input/output instruments, linear notation is still used to manipulate the chemical structures. In developing languages for chemical reactions, line notation is preferrable since it provides unique representation of molecule and is convenient to apply.

1.2   Objective of Present Work

This work focuses on developing techniques for identifying side reactions in a chemical plant at the input-output block and recycle stages in the Douglas hierarchy. The approach taken reverts to earlier heuristic methods as described below. The present work does not attempt a rigorous representation of 'real' chemistry.

The idea behind this approach is that for many processes of potential industrial interest there is often a large amount of information available on the main reaction or reactions. The number of possible main reactions is relatively small and the plausible alternatives quite obvious. This suggests that applying automatic synthesis methods to discover main reactions is unlikely to be profitable.

Possible side reactions and their products are much less widely explored. There are many more of these than the main reactions, and there is normally little intrinsic interest in them. However, when a process is transferred from a bench scale batch operation to full scale, substances which were present in undetectable quantities, or which were never identified because their presence was never suspected, may appear in significant amounts. Futhermore, continuous operation, and in particular recycle, may cause build up of byproducts whose properties prevent their removal with identified byproducts or sidestreams.

Specific industrial examples of this situation are hard to come by, but anecdotal evidence suggests that the presence of such unexpected byproducts and their build up in recycle streams has been a problem for a number of novel processes. It is certainly cited as one of the reasons for undertaking extensive (and expensive) pilot plant studies.

1.3   Approach

Automated generation using an empirical but systematic approach requires the following facilities which were adapted from Nagel's modeling language for chemical reasoning[25].

   1. A means of defining chemical structures
      These are associated with structured formula, functional groups, atoms and bonds.

2. Definition of reactive behaviour of chemicals
   The reactive behaviour of chemicals is determined by functional groups which means the tendency of the atom bonds to cleave and form radicals.

3. Definition of reactions and pathways
   Reactions contain information about the species determining the reactants and the products. Pathways are the route taken to generate certain chemicals.

The method involves three main stages:

1. Species generation
   The generation of possible byproducts

2. Stoichiometric feasibility
   The identification of stoichiometrically feasible reactions leading to byproducts, and elimination of stoichiometrically infeasible byproducts

3. Thermodynamic feasibility
   Screening out those reactions which are thermodynamically unlikely under the proposed reaction conditions.

The work has been tested on a number of systems including :

- Partial wet oxidation of p-coumaric acid

- Alkylation of toluene with ethanol

- Vinyl chloride monomer process

- New refrigerants R134 and R22

1.4 Outcome

The outcome of this work is software for automated generation of chemical species and chemical reactions from specified initial reactants and automated evaluation of the chemical reactions. The program uses recursive exploration of species generation until all the possible structures are revealed. It provides the user with a number of possibilities to be selected from. Results obtained from this method are then compared to the experimental work presented by other workers.

The outcomes are displayed in a tree-graph format where reaction pathways and species can be viewed. This method can be used not only to study side reactions in a chemical process but also in finding alternative mechanisms.

1.5 Structure of Thesis

The thesis is structured as follows; Chapter 2 contains literature background, method is described in Chapter 3, application of the method with results are given in Chapter 4 and 5, conclusions and recommendations are presented in Chapter 6.

Chapter 2

Literature Survey

This chapter provides information on the state of the art of reaction path synthesis and related work. The latter includes the evolution of computerised molecular representation for the purposes of building up chemical database and retrieval of components.

2.1 Introduction to Reaction Path Synthesis

The reaction path synthesis task may be described using two concepts; the net reaction and the intermediate reactions. The net reaction is the single step overall reaction containing initial and final species which is normally infeasible. The net reaction which is also called the main reaction is the one to produce finish material that is stoichiometrically feasible but not thermodynamically. The net reaction is thus replaced by several intermediate reactions. The intermediate reactions are the feasible reactions which act as intermediary converting the initial species into the final species. The production and consumption of the intermediate species must conform with the law of mass conservation. The material produced in one reaction has to be consumed at the same amount in another reaction. The sequence should end up in a closed cycle giving zero net for the intermediates[6].

Strategic formulation of the reaction paths was first considered by Rudd and May[6] for the soda ash process using graph theory to represent the behaviour of chemical reactions. The reactions involved in the making of soda ash is well known as a Solvay cluster as the name of the person who discovered it. Hence, a sequence of reactions built up by several reactions contributing to the production of certain chemical and yet may not directly related to the initial or the final species is referred to Solvay cluster[6, 7]. The concept of the Solvay cluster has been applied to the manufacture of a range of industrial products such as sulfuric acid, carbon tetrachloride and ethyl ether[8] and also in mineral and electrochemical processes. It focuses on generating feasible intermediate reactions to replace the infeasible net reaction. Driven by the need for more effective methods and different application, researchers have come with different approaches, such as mathematical and algebraic approach[9], methodology for environmental impact minimization[11, 13] and the application of recursive satisfaction of constraints[14]. Pragmatic definition for quick estimation has also been applied for

industrial practice[20].

Recently, work on reaction pathway synthesis have been influenced by methods originated in other areas especially computer science and artificial intelligence. The influence of mechanistic studies of biochemistry and catalysis has brought research back to synthesizing detailed chemical reaction networks including detailed molecular transformation, molecular modelling and molecular kinetics[31]. Consequently, this area has evolved from simplified reaction synthesis to creating representation of molecules combined with the synthesis of complex reaction paths.

Work on the development of chemical language covered both chemical representation and reaction networks and laid the foundation for a more comprehensive work in chemical reaction synthesis. Qualitative reasoning is applied to generate chemical reaction language called LCR (Language for Chemical Reactions)[24, 25]. A generic computer language (Reaction Description Language) based on reaction mechanisms has also been developed[32, 33]. The objective is to provide a generic computer language that allows flexibility in the generation of the types of molecules and reactions. The reason for this development is that current challenges in chemical reaction generation cannot be met with ordinary models. Design and operation of chemical processes have been faced with increasing competitiveness in the product quality requirements and environmental regulations. Therefore improving models of molecular transformations is required.

The following section illustrates several examples of reaction clusters.

2.2 Examples of reaction clusters

2.2.1 Soda ash processes

The net reaction of the soda ash process is infeasible which is expressed in the following reaction :

$$2\ NaCl + CaCO_3 = Na_2CO_3 + CaCl_2$$
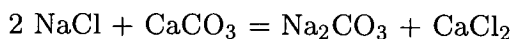
In the actual process, the production of natrium carbonate is governed by six intermediate feasible reactions.

$$
\begin{array}{ll}
CaCO_3 = CaO + CO_2 & 1000\ ^\circ C \\
CaO + H_2O = Ca(OH)_2 & 100\ ^\circ C \\
Ca(OH)_2 + 2\ NH_4Cl = CaCl_2 + 2\ NH_3 + 2\ H_2O & 120\ ^\circ C \\
2\ NH_3 + 2\ H_2O + 2\ CO_2 = 2\ NH_4HCO_3 & 60\ ^\circ C \\
2\ NH_4HCO_3 + 2\ NaCl = 2\ NaHCO_3 + 2\ NH_4Cl & 60\ ^\circ C \\
2\ NaHCO_3 = Na_2CO_3 + H_2O + CO_2 & 200\ ^\circ C
\end{array}
$$
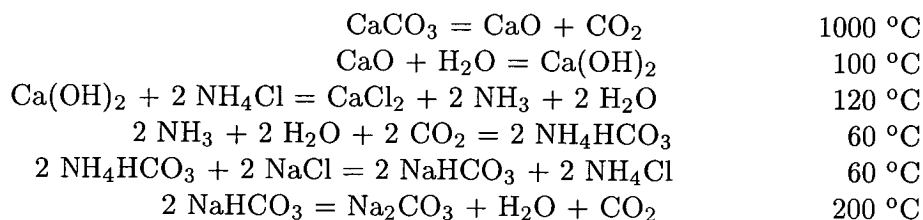
2.2.2   Potential reactions of nitrobenzene

The overall net reaction is :

$$C_6H_5 - NO_2 + 3H_2 \rightarrow C_6H_5 - NH_2 + 2H_2O$$
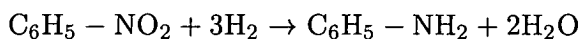
A cluster of potential reactions of nitrobenzene is found as follows :

$$C_6H_5NO_2 + H_2 \rightarrow C_6H_5NO + H_2O$$
$$C_6H_5NO + H_2 \rightarrow C_6H_5NHOH$$
$$C_6H_5NHOH + H_2 \rightarrow C_6H_5NH_2 + H_2O$$
$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5NH_2 + C_6H_5NO_2$$
$$C_6H_5NHOH \rightarrow C_6H_5N_2$$
$$\rightarrow (C_6H_5)_2N_2$$
$$C_6H_5NO_2 \rightarrow decomposition\ products$$
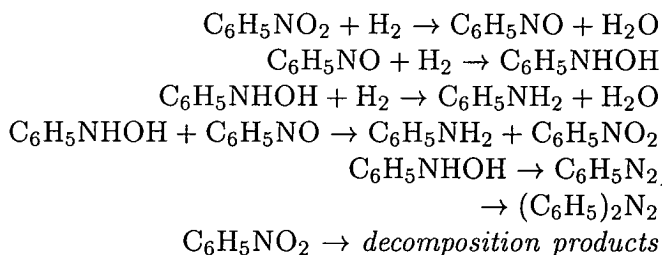
2.2.3   Styrene production

The reaction path for styrene production is used as an example in Douglas hierarchical approach.

- Process 1. Hydrodealkylation (HDA) of Toluene,   648 C, 34.01 atm, vapour phase
  $$C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$$
  $$2C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2$$

- Process 2. Ethylbenzene production,   426.67 C, 20.41 atm, vapour phase
  $$C_6H_6 + C_2H_4 \rightarrow C_8H_{10}$$
  $$C_8H_{10} + C_2H_4 \rightleftharpoons C_{10}H_{14}$$
  $$C_{10}H_{14} + C_2H_4 \rightleftharpoons C_{12}H_{18}$$

- Process 3. Styrene production,   601.67 C, 1.70 atm, vapour phase
  $$C_8H_{10} \rightleftharpoons C_8H_8 + H_2$$
  $$C_8H_{10} \rightarrow C_6H_6 + C_2H_4$$
  $$C_8H_{10} + H_2 \rightarrow C_7H_8 + CH_4$$

Chemical formulae and names :
C_6H_6 = benzene
C_7H_8 = toluene
C_8H_8 = styrene
C_8H_{10} = ethylbenzene
$C_{10}H_{14}$ = diethylbenzene
$C_{12}H_{10}$ = diphenyl
$C_{12}H_{18}$ = triethylbenzene

2.3 Synthesis of reaction paths

The following section consists of methods on the synthesis of reaction paths developed by other workers.

2.3.1 Graph theory for intermediate reaction development

May and Rudd[6] proposed a graphical approach to analyze Solvay clusters. In this work, reactions are represented in a polygon of acyclic directed graph where the intermediate reactions nest inside the net reaction. The polygon also represents the balanced stoichiometry of the reactions. Reactants are shown in clockwise direction and given negative values, while products are shown in the opposite direction and given positive values. Intermediate reactions inside the polygon create regions equal to the number of the reactions. The original Solvay cluster in the making of soda ash is used to illustrate the method. See Figure 2.1.

The infeasible net reaction of the soda ash is as follows :

$$2\,NaCl + CaCO_3 = Na_2CO_3 + CaCl_2$$
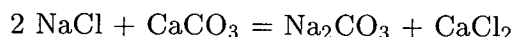
Six intermediate reactions replacing the infeasibility were created.

$$
\begin{aligned}
CaCO_3 &= CaO + CO_2 & 1000\ ^\circ C \\
CaO + H_2O &= Ca(OH)_2 & 100\ ^\circ C \\
Ca(OH)_2 + 2\,NH_4Cl &= CaCl_2 + 2\,NH_3 + 2\,H_2O & 120\ ^\circ C \\
2\,NH_3 + 2\,H_2O + 2\,CO_2 &= 2\,NH_4HCO_3 & 60\ ^\circ C \\
2\,NH_4HCO_3 + 2\,NaCl &= 2\,NaHCO_3 + 2\,NH_4Cl & 60\ ^\circ C \\
2\,NaHCO_3 &= Na_2CO_3 + H_2O + CO_2 & 200\ ^\circ C
\end{aligned}
$$

1. Polygon representation of reaction A + B = Z

2. The nested polygons of the Solvay cluster :
   A + L = N
   N + B = Z + L

3. Solvay soda ash process :

CaCO3 = CaO + CO2
CaO + H2O = Ca(OH)2
Ca(OH)2 + 2 NH4Cl = CaCl2 + 2 NH3 + 2H2O
NH3 + 2 H2O +2 CO2 = 2 NH4HCO3
2 NH4HCO3 + 2 NaCl = 2 NaHCO3 + 2 NH4Cl
2 NaHCO3 = Na2CO3 + H2O + CO2

Figure 2.1: Graphical representation of Solvay clusters

May and Rudd stated the criteria to identify useful sequences. The individual reaction should convert at a reasonable high rate at industrial operating conditions with sufficient yield, safety, and economy. Three conditions must be met, i.e.

- the stoichiometry consistency

- theoretical equilibrium condition which must guarantee the formation of products

- high rate reaction

Although it is necessary that the chemical equilibrium resides with the products, it is generally agreed that for a reaction to be commercially feasible, its Gibbs free energy changes must be less than 10 kcal/mol. Consequently, this condition results in the equilibrium yields less than a few percent and thus requires extensive separation and recycle systems. May and Rudd used 10 kcal/mol as the reactions' feasibility criteria.

To analyze the thermodynamic feasibility, reactions which fulfill the stoichiometric criterion are depicted in a G-T diagram (free energy - temperature diagram). The thermodynamic criterion is analyzed using the concept of common differences. A common difference is a component common for each reaction. The common difference between reactions is the common edge in the polygon representation. Reactions having the same common difference are plotted in a G-T diagram which then give a ladder pattern. The patterns would indicate an integration between stoichiometric and thermodynamic feasibility. For reactions shown below, the G-T diagram is depicted in Figure 2.2. Temperature is taken as variable that defines the reaction conditions on which the reactions must be run. The free energy of the N-L line must be closed or crossing that of the A line and Z-B line. If such conditions cannot be found then the proposed Solvay cluster is not feasible.

$$
\begin{array}{lll}
\text{net :} & A + B = Z & Z - B = A \\
\text{reaction(1) :} & A + L = N & N - L = A \\
\text{reaction(2) :} & B + N = L + Z & N - L = Z - B = A
\end{array}
$$
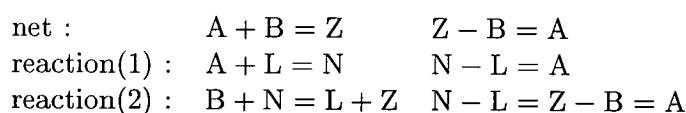
By rearranging the equations, the common difference is then found as A. The left hand side of the equations is called the half reaction. The ladder pattern also shows the differences of free energy ('e') which must be less than or equal to 10 kcal/mol.

If it is not apparent as to which related compound to get started with, an artificial common difference is introduced. Artifical common difference is a theoretical tool for the construction of an expanded set of clusters. It is created by introducing a new intermediate species into the polygon. For example, in the search of Solvay cluster to replace the infeasible reaction of hydrogen chloride decomposition, the H_2O decomposition reaction to H_2 and O_2 is introduced. This would give $\frac{1}{2}O_2$ as the common difference which is artifical to the original problem. The original problem has Cl_2 as the common difference. Therefore there would be many more alternatives of half reactions available which lead to the finding of reaction pathway. The artificial common edge does not need to appear in the final Solvay cluster. Other examples of these components are halogens, sulfur and components which are commonly found in
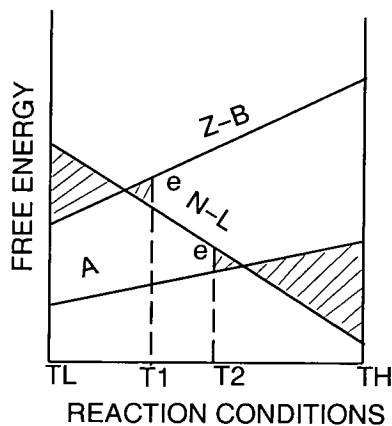
Figure 2.2: The ladder pattern for thermodynamically feasible Solvay clusters

the chemical industries. The concept is later extended to multiple common difference when there is no feasible path on the G-T diagram that leads from reactants to products. The multiple common difference combines two reaction sets which might produce a lot more new half reactions.

The properties of the May-Rudd polygons in relation with the accessibility of the Solvay cluster are explained in more detailed in a subsequent paper by Rudd[7]. He concluded that there is no limit to the size of the clusters that can be synthesized provided that they have planar topological structure. Planar here means that there is no crossing of line in the May-Rudd polygon.

The above studies demonstrate the practical aspect of graphical representation to guide the selection of closed cycle reaction sequences that satisfy Gibbs free energy constraint. Although it has been found that the method is effective to solve unlimited number of clusters, but it may become a daunting task when employed to solve more complex problems.

As for the economic feasibility, each synthesized feasible cluster must be further analyzed for its efficiency in energy use, selectivity of reactions, reaction rates and choices of the separation. The work described here is the first effort to formulate the behaviour of Solvay cluster.

2.3.2 Mathematical/Algebraic Approach

An algebraic approach presented by Rotstein and coworkers[9] is used as an analytical framework to synthesize a cluster of reactions given a set of permissible chemicals. This work is similar to the ladder pattern in May-Rudd G,T diagram in approach, but Rotstein improves the concept by adding an algebraic formulation called q line as an indicating parameter in G,T diagram. The q line will enable the exploration of more alternative species based on pattern recognition to identify the thermodynamically

feasible and unfeasible regions. The analysis concerns with single-step and multistep reactions including open and closed sequences of reactions (clusters).

In this method, an atom balance equation of a chemical reaction in a closed system introduced into the Gibbs free energy equation. The procedures provide invariants of algebraic properties of chemical reactions in the space of free energy change and temperature. The production of certain chemical products is searched by shifting the unfeasible region into the feasible one or substituting chemicals in the atomic matrix. The characteristics of the systems are formulated in an equation shown below.

The following expression is the free energy equation of a chemical reaction of s species and p products as a function of temperature. This temperature indicates the operating condition required. Parameter q represents the amount of chemicals involved in the span of the bounded region and outside it. The species must be listed in order, and an infinite number of reactions can be generated by specifying one of the stoichiometric coefficients of the species is equal to q. In the following equation, species s, that is the species before the desired product (p) is given a stoichiometric coefficient equals q.

$$\Delta G_{rT}^0 = -q\alpha_{(s-1)}^T a_\epsilon - \alpha_{(s-1)}^T b_\epsilon + \alpha_s q + \alpha_p + [-q\beta_{(s-1)}^T \alpha_\epsilon - \beta_{(s-1)}^T b_\epsilon + \beta_s q + \beta_p]T$$

where :
   α_p and β_p are product constant, with stoichiometric coefficient 1
   chemical s with constants α_s and β_s with stoichiometric coefficient q
   (s-1) chemicals with constants α_{s-1} and β_{s-1} with stoichiometric -
   coefficient ν_{s-1}

$$\nu_{s-1} = -qa_\epsilon - b_\epsilon$$

Or the above equation can be shortened as follows :

$$\Delta G_{rT}^0 = (\alpha + \beta T)^T \nu$$

where α and β are vectors of thermodynamic constants for all chemicals and ν is the vector of all stoichiometric coefficients.

The equation proves a series of properties possessed by various chemical reactions in the $\Delta G, T$ space, see Figure 2.3.

1. Any two lines $\Delta G(T, q)$ will intersect at a point $(\Delta G_+, T_+)$. The intersection point of T_+ depends on the atomic structure and properties of all the chemicals involved but the product, while ΔG_+ depends on all chemicals.

2. Substitution of the product chemical by a different one results in a shift of the common point $(\Delta G_+, T_+)$ parallel to the ΔG_{rT}^0 axis at constant T.

3. The $q = 0$ line in a ΔG_{rT}^0 vs T chart has a slope which is independent of the ϵ_s vector (the chemicals s) which means that the chemicals s will not be a part of

the reaction and since the product stoichiometric coefficient is specified, there will be a unique solution provided condition of the rank of the atomic and element matrices (e), $r_e = r_a = s$, is satisfied. For $q = \infty$, it is unlikely that s being a by-product or raw material which appears in infinite amount.

4. If the $(\Delta G_+, T_+)$ point is interior to **R**, the reaction is feasible.

5. Substitution of a new chemical for one of those of the subset of s chemicals results in a shift along a straight line towards a new $(\Delta G_+, T_+)$ point.

6. The value of T_+ does not change when the chemical s is interchanged with any $k \leq s - 1$ chemicals, provided that the interchange does not lead to a set in which $det(\underline{\varepsilon}_{(s-1)}) = 0$.

7. When the new chemicals that substitute one chemical belong to a homologous series, in general, they sequence themselves so that ΔG_+ decreases as the carbon content decreases.

In addition to that, the feasibility criteria must also be satisfied by the number of chemical reactions among the chemicals. They are determined by the relationship of the rank of the atomic matrix (r_a) and the rank of $(e * s)$ matrix (r_e). For an infinite number of feasible reactions to exist, $r_a = r_e = c < s$, if $r_a > r_e$ then there is no feasible reaction.
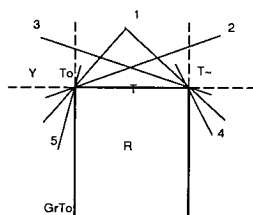
Region R is the feasible region in corresponding with
To and T~ and GrTo < Y
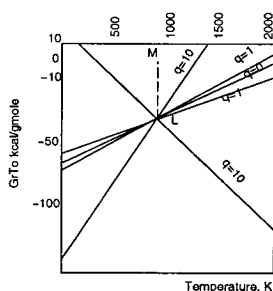
The value of T+ does not depend on the final product (butadiene).
L is the intersection point when the product is butadiene
and the other intervening chemicals are carbon monoxide,
ethanol, acetylene and acetal dehyde.
M is the intersention point when propylene is the products.

Figure 2.3: The reaction characteristics in G-T space

The procedures are illustrated using a single step reaction having a set of five species ($s = 4$ and $p = 1$). The species comprise carbon monoxide, butadiene, acetylene, acetaldehyde and o-xylene. O-xylene is the final product (p). The bounding temperatures

are set at $T_o = 200$ K and $T_\infty = 2000$ K. Using the above G, T equation and diagram, for the q line to intersect the line at $\Delta G^o_{rT} = 10$ kcal/gmole, there would be a maximum value of $q = 1.66$. This also indicates that the limited range of the acetaldehyde byproduct is between 0 and 1.66. This corresponds to $\nu_a =$ (-1.66, -3.49, 2.15, 1.66, 1)^T resulting in the following chemical reaction :

$$1.66 \ CO + 3.49 \ C_4H_6 = 2.15 \ C_2H_2 + 1.66 \ CH_3CHO + C_6H_4(CH_3)_2$$
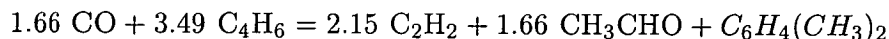
When carbon monoxide is subsequently replaced by butanol, propanol, ethanol, methanol, formaldehyde and water, the points shifted accordingly and produced different results. For example, if CO is replaced by water, then the resulting coefficients would be :

$$2.00 \ H_2O + 1.0 \ C_4H_6 + 1.0 \ C_2H_2 = 2.0 \ CH_3CHO + 1.0 \ C_6H_4(CH_3)_2$$
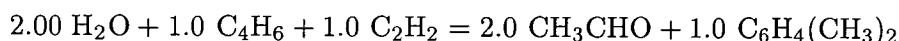
The results show that topological properties of the chemical reactions in the $\Delta G, T$ space can be used to generate and screen alternative feasible chemical reactions. Although this method seems to increase the possibilities to find alternative species, it is restricted by the number of species (s) which must be equal to the number of elements (e) plus one. With this restriction, it can be quite cumbersome if the problem involves a mixture of complex species.

A similar concept is used in an attempt to broaden the scope of the problem but narrow the number of alternatives by analyzing the economic of the chemical reaction paths which has been done by Fornari and Stephanopoulos[10]. They consider Rotstein's work on atom balance in $\Delta G, T$ space as the starting point to systematic screening. The approach introduces economic parameters, such as positive added value requirements and meeting of demand and supply constraints.

The gross added value, V, is the difference between selling prices of products and byproducts and buying prices of raw materials which is calculated as follows :

$$V = \underline{v}_a^T \underline{p}$$

where $\underline{v}_a^T$ is the vector of stoichiometric coefficients and $\underline{p}$ is the vector of elements p_i that is the price of chemical i per mole of i.

The introduction of the gross added value influences the substitution of chemicals which is done systematically. For the screening test, the gross added value of the chemical having positive result must be large enough to accommodate all other cost items and an acceptable profit. Therefore,

$$V > 0$$

or in all probability

$$V > V_o$$

where V_o will depend on local conditions.

New alternatives are produced by systematic replacement of chemicals whose new gross added value will be given by :

$$V' = \underline{v}'^T_a \underline{p}'$$

When the degree of freedom is equal to 1 ($m = 1$) for all $V(q_s)$, there is a common intersection which corresponds to :

$$q_s^* = \frac{C_o - C_o'}{C_1 - C_1'}$$

Fig. 2.4 shows an example of the replacement of chemicals where CO, C_2H_5OH, CH_3CHO, C_2H_2 and C_4H_6 are the set of the starting point (case 1). C_4H_6 is the desired product. Case 2 and 3 are the first column vector successively replaced by H_2O and HCOH. Case 1 has a negative gross added values and case 3 is the most promising one shown by the highest value.
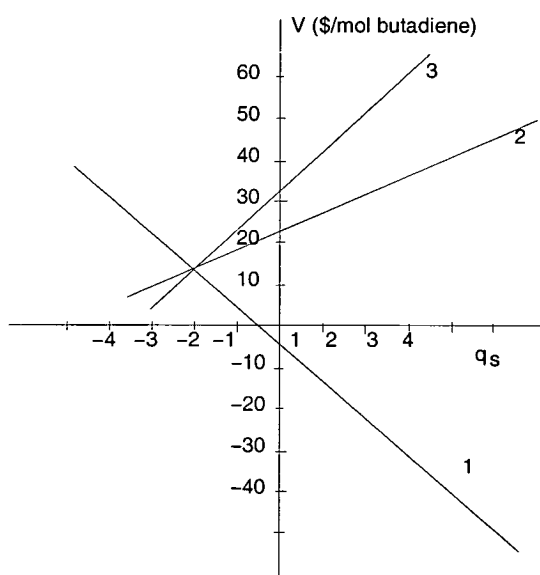
Figure 2.4: Illustration of component replacement having case 1 as the starting set

The procedures were also applied for identifying the role of species, whether it is more profitable to have a species as a reactant or as a product. This subsequently has a relation to supply and demand constraints. If a chemical is to be a raw material, then it is subject to supply constraints, likewise if a chemical is to be a product then it must be produced as much as the demand states. All these variables were incorporated in the mathematical formulae shown above.

The results of these studies demonstrate that the introduction of economic parameters into the chemical selection would provide insight into more profitable chemicals to be

produced. The algebraic approach significantly broadens the scope of the problem space. More alternatives species having various conditions could be investigated more quickly. However, since this method is an extended procedures of Rotstein's work, it is restricted by the relation between the number of species and the number of elements involved. Beside that, considering economic parameters at this stage might not give a siginificant impact to the final process design. Chemical prices could only be a small percentage of the overall investment cost.

2.3.3   Environmental Impact Minimization

Design of reaction paths for minimizing environmental impact has been presented by Buxton et al[11]. The method is aimed at generating a set of alternative reaction routes to achieve a desired product. The process technology must be commercially viable and have minimum environmental impact.

The procedures outlined in this work introduce a key step where 'co-material' group is selected and the candidate 'co-materials' are determined using group based molecular design technique. The 'co-materials' are group structures which are expected to be present in the desired product. The next step is identifying the stoichiometries using logic based representation systems and optimization selection incorporating aspects of the MEIM (methodology for environmental impact minimization). Competing reactions are generated by creating reaction mechanisms through functional group transformations. The mechanism steps are finally evaluated in detail using MEIM[12].

The construction of 'co-materials' is restricted by several rules, e.g. groups must be present either in the product, the existing raw materials, co-products or by-products. Groups may not violate environmental restriction such as chloro groups and also must be set for the desired chemistry such as aromatic or cyclic. The introduction of the co-material generation into the procedures reduces the problem space considerably. The stoichiometric coefficient in relation with economic and thermodynamic constraint is determined by optimization procedure formulated in a mixed-integer non linear programming. The objective is to minimize the environmental impact by measuring it in terms of the critical water mass (CTWM). CTWM commonly used to assess environmental impact is the mass ratio of water pollutant to standard limit value in water[12].

This method is illustrated using the production of 1-naphthalenyl methyl carbamate (carbaryl) which was employed as a pesticide and was manufactured by Union Carbide. The raw materials of the Union Carbide's process consist of 1-naphthol and methyl isocyanate. Methyl isocyanate is a very toxic substance and in fact can be eliminated from the process. An alternative route to produce carbaryl is by reacting 1-naphthol and phosgene to generate 1-naphthalenyl chloroformate as an intermediate. This compound reacts with methyl amine to produce carbaryl. The assessments begin with functional group selection procedures, some aromatic and aliphatic groups as groups of interest are selected. Hence, 'co-material' design synthesis results in the possible use of 15 components, such as naphthalene, 1-chloronaphthalene,

1-naphthol, carbaryl, chlorine, methyl chloride, methyl isocyanate, phosgene and so on. Stoichiometric analysis is employed to select feasible reactions followed by equilibrium, economic and environmental impact analysis. The results show that the alternative route is more promising in terms of economic and environmental impact.

The procedures illustrated in this paper suggest that by incorporating other factors especially evironmental impact, alternative reaction paths can be designed. Therefore the use of toxic materials can be avoided. As the method employs group contribution, the procedures seem much simpler for it can give direct determination of material properties.

Stefanis et al[13] used MEIM for solvent selection and reaction path synthesis. The procedures consist of three steps, i.e.

1. The identification of all agent-based operations within the process interest and specification of performance constraints for each separation task.

2. At the separation task level, the determination of a list of candidate solvents satisfying processing and environmental constraints.

3. At the process level, the selection of optimal solvent (from the list) based on global plant-wide process and environmental constraints.

In this discussion, the task is limited to the separation level with the following problem definition.

- a multi component stream of fixed flowrate and composition

- a specified separation task with fixed operating condition

- a set of constituent structural groups (e.g. $-CH_3$, -CHO, ...) and their associated group constristion parameters

- the type of agent molecule required (acyclic, monocyclic or bicyclic)

- minimum composition approach for each pair of process/agent streams, so as to ensure feasible mass transfer, then the objective is to design a set of feasible agent molecule structure(s) featuring optimal separation performance and minimum environmental impact.

The performance indicator can be :

- solvent capacity - defined as the ratio of the solute exit fractions in the solute lean and rich phase respectively

- solvent loss

- environmental impact metrics (critical air mass or critical water mass)

The procedures are illustrated in a gas absorption task to recover acetaldehyde (CH_3CHO) from a mixture of 68 % mol acetaldehyde, 23 % mol ethylene and 9 % mol oxygen of 146.5 kgmoles/h (at 310 K and 2 atm). Candidate structural groups are as follows :

$-CH_3, -CH_2, > CH-, > C <, -OH, H_2O, -COCH_2, CH_3COO-,$
$-CH_2COO-, CH_3O-, -CH_2O-, > CHO-, -COCH_3, -CHO, ArCH, ArC,$
$ArC - CH_3, ArC - CH_2, ArC - CH, ArC - OH, ArC - Cl$

Two different types of molecular structures are considered, i.e. acyclic and monocyclic aromatic. The assessments provide 4 most favourable candidates: water, methanol, acetone and phenol. These solvents are then examined at the global plant level incorporating plant operational aspects. The results show that water is the most favourable solvent due to its low cost, while acetone is the most expensive. On the other hand, acetone has the lowest environmental impact and energy requirements. Methanol is the most environmentally benign while having slightly more expensive recovery cost than water, and thus the best solution.

In reaction path analysis, there are two possible routes for the production of acetaldehyde, that is ethylene oxidation and ethanol dehydrogenation. By defining the material states and reaction tasks, the problem is then posed in a mixed integer optimization involving mass balance around the state nodes and the task nodes, energy equations and cost and environmental impact functions. The results show that the use of ethanol dehydrogenation is more promising in terms of less material and power wastes. For global minimum wastes, the ethylene route is more favourable since the input waste of the ethanol route dominates over the other factors.

This method is useful in selecting chemicals to be used as solvents and finding profitable routes. However, the application of the method is limited due to a very focussed aim that is waste reduction.

2.3.4 The Application of Recursive Satisfaction of Constraints

Symbolic and quantitative reasoning has been applied to compose reaction pathways from a set of elementary reactions (Mavrovouniotis[14]). The synthesis is concerned with satisfying a number of constraints imposed on artifacts. Artifacts in this context are the mechanisms of catalytic reactions or pathways of ordinary reactions. The procedures are recursive, infeasible elementary reactions are eliminated in succession until feasible pathways are determined. The constraints consist of definition of starting materials and final products and steps of reactions meeting stoichiometry and equilibrium criteria.

In developing the method, Mavrovouniotis adopted the procedures developed by Happel & Sellers[15], Happel et al[16] in a mechanistic study of chemical reactions with catalysis. A unique set of mechanisms in a heterogeneous catalytic system can be determined by specifying an initial choice of elementary reactions, intermediate species and terminal species. Elementary reactions are irreducible consisting of basic

molecular transformations, which include all possible reactions of ions or active surface site of catalysts in heterogeneous systems or formation of radicals in homogeneous reactions. Intermediate species are those which must be consumed and not appear in the net reaction, while terminal species constitute raw materials and products. An overall mechanism is achieved by combining elementary reactions in specific proportions, such that the intermediate species do not appear. In establishing a mechanism, Mavrovouniotis & Stephanopoulos[17, 18] defined a directionality term such that a direct mechanism is an overall mechanism includes all the correct direction of irreversible steps. In their procedures, they considered elementary steps as partial mechanisms.

The algorithm works by selecting an intermediate species to be eliminated first. The elimination is carried out by combining two or more elementary steps containing the species, creating a set of new mechanisms. The next species to be eliminated is then chosen and the procedures are repeated. The algorithm terminates when there is no more intermediates to be eliminated. The construction of new mechanisms by combinatorial process might lead to complex and multiple occurences. Therefore, by carefully selecting the species to be eliminated, the complexity of the program could be reduced as the number of combinations of the elementary steps are minimized. Redundancies are checked and deleted in the end.

The method described here is used for the synthesis of biochemical production routes. The mechanism steps are translated as individual bioreactions, usually catalyzed by enzymes. Overall reaction mechanisms correspond to acceptable biochemical pathways for a bioprocess. The procedures are applied in the synthesis of biochemical production routes which are described in the following section.

The development of reaction paths through synthesis of biochemical production routes was presented by Mavrovouniotis and Stephanopoulos[19]. Their work deals with techniques to generate systematic synthesis for reactions involving microorganisms satisfying linear stoichiometric constraints. The approach taken here is different from that of non-bioprocesses. In this study, the species is called metabolite and the reaction is called bioreaction, and these can be defined as having different roles depending on the pathways. The procedures consist of pathway construction meeting certain specifications (so-called metabolites' role), from a set of enzyme-catalyzed bioreactions whose stoichiometry is given. The specifications may include metabolites required as final products of the pathway, metabolites as reactants and bioreactions prohibited from participating in the pathway. Bioreactions constraints consist of reactions participate in forward direction and those participate in reverse direction. All these reactions must satisfy thermodynamic constraint. In order to construct pathways from bioreactions, database of metabolites and bioreactions are needed.

The problem is formulated as follows :

- Each metabolite can participate in the pathway in any of the following 3 capacities: a net reactant or substrate, a net product and an intermediate.

- One-step pathways obtained from the loose constraints of bioreactions are as-

sembled generating lists of pathways that produce metabolites (L_p), consume metabolites (L_c), metabolites as intermediates (L_r), non-participating metabolites (L_n) and a combination of one pathway from L_p and one pathway from L_c.

- The new set of active pathways is constructed by applying the metabolite constraints.

The number of pathways generated by combinations of constraints can grow exponentially. This computational complexity is thus avoided by investigating the structure of biochemical networks so as the number of active pathways can be maintained at low level. Structural exploitation can be made because metabolic reaction networks contain isolated linear pathways for special products and connected only sparsely with the intermediate metabolism. If a compound is an excluded product and cannot be recycled, then the entire chain can be discarded. If it can be recycled then the whole reactions that produces the compound are treated as a single pathway.

The method is illustrated using serine synthesis having the following stoichiometric specifications: the required reactant is glucose, the required product serine, the allowed reactant is ammonia and the allowed product is carbon dioxide. Allowed reactants and allowed products consist of oxidation-reduction currency metabolites, direct energy currency metabolites, indirect energy-currency metabolites and co-enzymes. Species of this category are AcCoA (acetyl-coenzyme-A), Mal (malate), phosphate (Pi) and so on. At first these species are omitted from the problem specification because they are always designated as in this category. However, in this case, the program cannot run without one, or in other cases the program might run forever. By introducing one or a few of the species from the last category, the program runs to completion. Several alternatives of reaction networks can be produced.

The synthesis of reaction paths for biochemical production requires database on elementary reactions and well formulated problem to gain a satisfactory computational performance. The method described here depends heavily on the database containing the species and reaction constraints.

2.4 The Use of Reaction Paths in Process Synthesis

2.4.1 Heuristic Development Using A Hierarchical Approach

The synthesis of multistep reaction processes carried out by Douglas[20] shows how the reaction paths dominate the selection of the connectivity of reactor systems and separators. Simple rules based on the chemistry of the process are developed to guide the generation of process alternatives. Identification of the best few alternatives is done by applying cost estimation.

In making commodity chemicals such as monomers, pesticides and so on, a large number of reactions are proposed, and the production and consumption of the intermediates must be properly designed because they are not available in the market. To facilitate

the need, a new plant ought to be built. A given chemistry process with an estimate of the production rate, product distribution and raw material is not always sufficient for a conceptual (preliminary) design. The process units and their interconnectivity have to be selected and the dominant design variables have to be identified to enable the estimation of the optimum design condition. The procedures addressed in this paper are limited to a pragmatic definition for quick estimation in industrial practice rather than a broader and complete definition. Douglas states that the best alternatives for further consideration are determined at the earliest level, and then more detail and more accuracy are added as the project progresses through the levels. In general, the design problems fall into six categories, ie.

1. Operation : continous or batch

2. Product slate : single, multiproduct and multipurpose

3. Product characteristic : pure, mixture

4. Phases : vapour, liquid, solid

5. Industrial grouping : petrochemical, agricultural chemicals

6. Underlying science : organic, inorganic

The synthesis of styrene production and bis-hydroxyl-ethyl terephtalate (BHET) below are used as examples in the decision making procedures. The reaction path for styrene production is based on the common route. The BHET process is made by ammoxidation of p-xylene which is a new chemical route instead of air oxidation of p-xylene. In normal process, terephthalic acid is produced first by air oxidation of p-xylene, which causes loss of p-xylene due to its conversion to CO_2 and H_2O. Ammoxidation of p-xylene produces terephthalonitrile (TPN), and by setting the ratio of ammonia to p-xylene at 4, the selectivity to terephthalonitrile (TPN) can be increased to 0.954 and thus reduce the loss of valuable raw material.

1. Styrene production

   - Process 1. Hydrodealkylation (HDA) of Toluene,   648 °C, 34.01 atm, vapour phase
     $C_7H_8 + H_2 \rightarrow C_6H_6 + CH_4$
     $2\,C_6H_6 \rightleftharpoons C_{12}H_{10} + H_2$

   - Process 2. Ethylbenzene production,   426.67 °C, 20.41 atm, vapour phase
     $C_6H_6 + C_2H_4 \rightarrow C_8H_{10}$
     $C_8H_{10} + C_2H_4 \rightleftharpoons C_{10}H_{14}$
     $C_{10}H_{14} + C_2H_4 \rightleftharpoons C_{12}H_{18}$

   - Process 3. Styrene production,   601.67 °C, 1.70 atm, vapour phase
     $C_8H_{10} \rightleftharpoons C_8H_8 + H_2$
     $C_8H_{10} \rightarrow C_6H_6 + C_2H_4$
     $C_8H_{10} + H_2 \rightarrow C_7H_8 + CH_4$

2. Bis Hydroxyl Ethyl Terephtalate (BHET)

- Process 1. Terephthalonitrile (TPN) production,   690 °C, 1.77 atm, vapour/solid

$$p-C_8H_{10} + NH_3 + 3\ V_2O_5 \rightleftharpoons C_8H_7N + 3\ H_2O + 3\ V_2O_4$$
$$C_8H_7N + NH_3 + 3\ V_2O_5 \rightleftharpoons C_8H_4N_2 + 3\ H_2O + 3\ V_2O_4$$
$$p-C_8H_{10} + 21\ V_2O_5 \rightleftharpoons 8\ CO_2 + 5\ H_2O + 21\ V_2O_4$$

  If NH_3 / p-Xylene = 4; Selectivity to TPN = 0.954

- Process 2. Catalyst recovery,   690 °C, 1.77 atm, vapour/solid

$$V_2O_4 + \tfrac{12}{O}_2 \rightleftharpoons V_2O_5$$

- Process 3. Bis-hydroxy-ethyl terephtalate (BHET) production   200 °C, 1.02 atm, vapour phase

$$C_8H_4N_2 + 2\ C_2H_6O_2 + 2\ H_2O \rightleftharpoons C_{12}H_{14}O_6 + 2\ NH_3$$

Chemical formulae and names :
$C_2H_6O_2$ = ethylene glycol
C_8H_{10} = o-xylene, p-xylene
C_8H_7N = p-tolunitrile (TN)
$C_8H_4N_2$ = terephthalonitrile (TPN)
$C_8H_6O_4$ = terephtalic acid (TPA)
$C_{12}H_{14}O_6$ = bis-hydroxy-ethyl terephtalate (BHET)
$C_{10}H_{10}O_4$ = dimethyl terephtalate

Intermediate chemicals such as benzene and ethyl benzene in the styrene production are available in the market, so the integrated process that produces the intermediate chemicals and the product (styrene) is called a plant complex. The intermediates in BHET production process are not obtainable in the market, so the plant that makes the product has to produce them. This type of process is called a multistep reaction process, although it is still considered as a plant complex. A multistep reaction process is much more complex than an integrated process and the hierarchical design procedure has to be revised and broken down into sub levels.

A multistep reaction process requires a complex plant which is then decomposed into smaller plants so that they are simple and easy to understand and solve. All reactions that take place in the same temperature or pressure are grouped together, as well as that of the recovery system to recover certain material. The plant connectivity is also determined by the plant chemistry, i.e. the plant where certain material has to be separated and consumed as reactant in another plant.

Therefore, based on the above classification, the determination of the input/output structure of the plant in level 2 proceeds. In the styrene plant, it is desirable to recover benzene from the third plant (styrene) and recycle it to the second plant (ethylbenzene) where it is a reactant. Similarly, it is more economical to recover NH_3 from the BHET plant and recycle it to the TPN plant. As for an illustration,

Figure 2.5 shows the connectivity of the BHET plant which has been examined by the chemisty of the BHET production process.
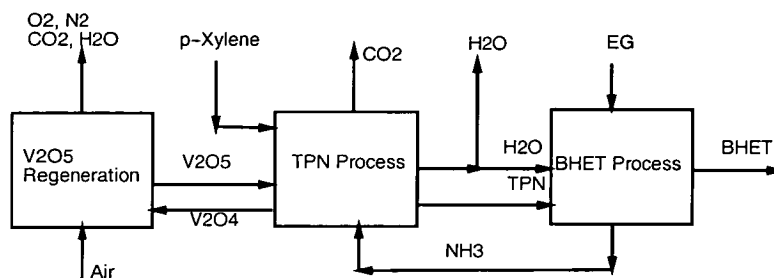
Figure 2.5: A schematic flowsheet for BHET Production

In connection with the above, generating flowsheet structure for multistep reactions has been studied by Phimister et al[21, 22]. In multistep reaction processes, successive or parallel chemical reaction occur in separate yet interconnected reactor-separator (RS) sections. The hierarchical decomposition approach used by Douglas is extended to analyze the multistep reactions. The proposed hierarchical procedures consists of the following steps :

1. Input information : continuous or batch, reaction paths etc.

2. Determination of reactor separator section connectivity

3. Reactor-separator input-output structure

4. Reactor-separator internal recycle structure

5. Separation section synthesis

6. Process energy integration

7. Analysis of alternative flowsheets

Phimister's work incorporates Douglas's level one and two to create a set of process topologies which are later transformed into chemical processes. In this study, the process topologies are created based on limited process information. The schemes of flowsheet generation start from a multistep chemical process. The problem is solved by viewing it as a graph, and using assumptions as follows :

1. Major chemicals likely to exist in the process

2. Generation of process kernel, i.e. the reactor-separator (RS) sections required in the process

3. Additional RS sections which may be present

4. Chemicals that must and must not enter or leave each section (component requirements)

5. Components' purposes in entering or leaving a section such as : reactant, product, byproduct, intermediate, coolant and so on (component purposes)

A requirement and purpose table is developed classifying components using assumptions 4 and 5 above. In conjunction with this table, a set of valid topologies are generated encompassing all desirable configurations. The individual component attributes must be exhibited in an RS section, it should be shown whether a chemical species must be present, must not be present or may be allowed in the section. There are also rules that have been developed to guide generation of component flowsheets, such as : the destination of the components leaving a section, a reactant in process feed must be connected to one or more entrances requiring that reactant and any product leaving a section must be connected directly to the process exit.

If the component requirements and purposes are not fulfilled, the structures constructed could be invalid and infeasible. Such component might be recycled back into the process and unable to leave. This will create build up of the components in the process line. In some cases, although the component requirements and purposes have been fulfilled, infeasible structures are still developed. Therefore it is advisable to implement additional pruning steps like reversibility or irreversibility of reactions.

Once the devoid flowsheets have been generated, flowheeting program package is applied to determine the compositions, temperatures and pressures, and material and energy balances of the process. This is followed by optimization procedures to analyze the generated structures resulting in useful assessements of the configurations. The method presented here is implemented in an existing chloromethane plant.

Integrating chemistry process with downstream design has also been studied by Miller and Davis[23]. They developed a system which is capable of getting chemical reaction information from process chemists and uses this information to determine process units to carry out the required functions. Cost analysis, environmental, regulatory and safety issues are taken into consideration at this stage. Therefore, the acceptable designs are those meeting satisfactory cost and safety assessments.

The syntax for chemical reaction input is in the form of process recipes, and the formalisms are according to the standard chemistry journals. The types of chemicals added and collected depend on the reaction path. Once the process topology is developed, critics are employed to evaluate particular aspect of design such as material and equipment issues. Critics are external to the system, but have access to the information. These critics provide feedback to the users regarding the process chemistry, and thus necessary improvement could be made.

The examples provided in this section show how the selection of reaction paths effect the plant connectivity (Douglas hierarchical approach). On the other hand, the economic of the process units and the interconnection of the systems may dictate the choice of a particular reaction route. In this instance, the losses of valuable raw materials are also taken into consideration. However, the plant chemistry presented

in this section is too general for identifying detail chemical reactions. It is rather concerned with the effect given to the design of a chemical plant by a determined reaction path.

Similar to Phimister's work, component based topologies affect the decision making of process flowsheet design. Detail definitions of components which exist or may exist in a process are required in order to validate the process topologies. This obviously relates to the choice of reaction paths. This study also indicates that the generation of major byproducts should be clearly defined and identified before hand, in addition to the main product, since the byproduct generation plays a crucial role in flowsheet design.

2.5   Automated Reaction Path Synthesis

2.5.1   Molecular Representation

The initial aim of the automation of molecular representation is to provide chemists with easy access to chemical database. A review on these early works (in the seventies) was written by Nishida[3], which focussed mainly on works with integrated approaches. He divided the techniques into two categories, that is :

- Logic Centred

- Direct Associative

Logic centred methods generate sets of intermediates which can be converted to target molecule by developing a synthetic tree, such as MATCHEM EROS by Ugi et al[26]. The program contains a very simple representation of chemical molecules based on the concept of isomerism. Rigorous mathematical models[27] using matrices were used for the foundation of various chemical reactions. The models were applicable for systems involving dissociated species, ions and other molecule fragments.

In MATCHEM EROS, chemical molecules are described by three parameters :

- the identity of every atom in the molecule

- the covalent bonds between atoms

- the free electrons for bonding at the outermost orbital of each atom

A molecule is decomposed into a set of atoms represented in a BE matrix (Bond-Electron connection matrix). A set of molecules is represented by a block diagonal matrix, where each sub matrix along the diagonal constitutes the representation of a set of atoms for the particular molecule, so called EM matrix (ensemble of molecule). If the molecules of an EM matrix do not react they retain their BE matrices, otherwise the EM-matrix is transformed by a linear operator R (reaction matrix) which denotes the way the molecules react with each other. The use of the rigorous mathematical formulation has resulted in significant and useful outcomes. See Figure 2.6 for an example.

The acetylene and hydrogen chloride reaction depicted in Figure 2.6 illustrates the procedure. The numbering codes at each atom denote the position of the particular atom in the molecule.

$$H1\text{-}C1\text{=}C2\text{-}H2 + H3\text{-}Cl1 \longrightarrow \begin{array}{c} H1\text{-}C1\text{=}C2\text{-}H2 \\ H3 \diagup \quad \diagdown Cl1 \end{array}$$

	H1	C1	C2	H2	H3	Cl1
H1	0	1	0	0	0	0
C1	1	0	3	0	0	0
C2	0	3	0	1	0	0
H2	0	0	1	0	0	0
H3	0	0	0	0	0	1
Cl1	0	0	0	0	1	0

BE (reactant)

+

	H1	C1	C2	H2	H3	Cl1
H1	0	0	0	0	0	0
C1	0	0	-1	0	1	0
C2	0	-1	0	0	0	1
H2	0	0	0	0	0	0
H3	0	1	0	0	0	-1
Cl1	0	0	1	0	-1	0

R

	H1	C1	C2	H2	H3	Cl1
H1	0	1	0	0	0	0
C1	1	0	2	0	1	0
C2	0	2	0	1	0	1
H2	0	0	1	0	0	0
H3	0	1	0	0	0	0
Cl1	0	0	1	0	0	0
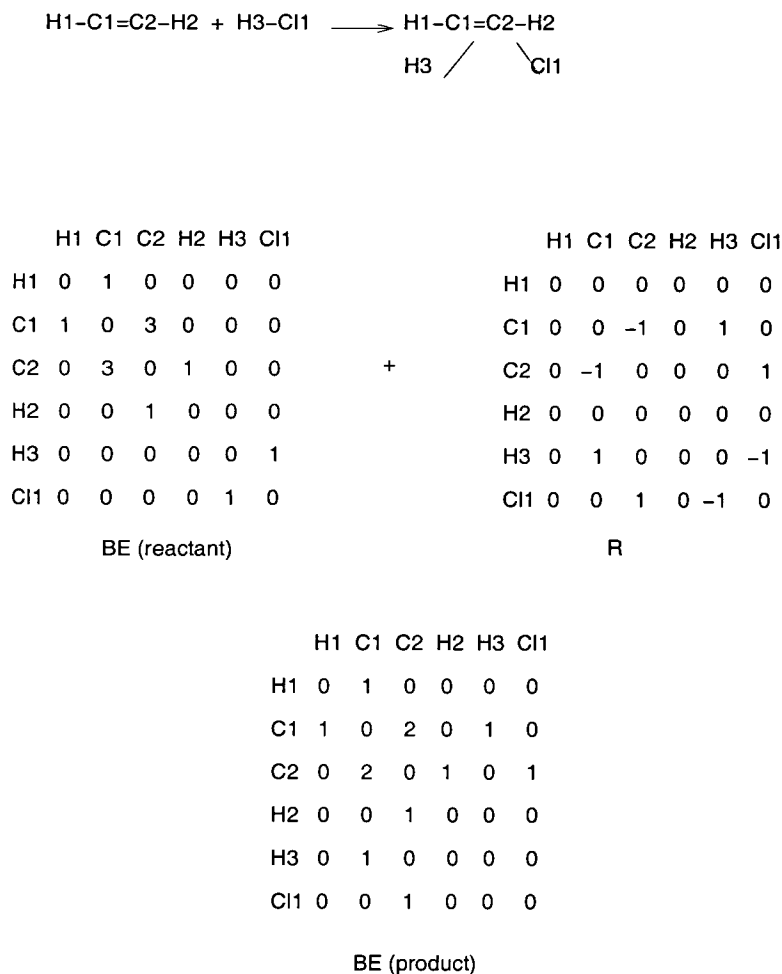
BE (product)

Figure 2.6: BE reactant and product and R matrices for acetylene and HCl reaction

Another method in this category is Hendrickson method (as mentioned in Nishida's review) which presents a constructive representation of chemical molecules. Parameters are divided into types of atoms contained in a molecule and topological structure of bonds. He identified four types of carbon sites and fifteen one step transformations which operate on one site. Operators are required to transform one organic molecule to another. The transformation of a single carbon site can occur in many ways which will lead to the development of a character triangle that identifies all possible states for a single carbon site. Consequently, it allows the enumeration of all possible states with large combinatorial problem. The transformation can be done either forwardly (synthetic) from the single element C to the target molecule or backwardly (retrosynthetic). To reduce the search space, Hendrickson introduced heuristics related to the type reactions involved. New reactions were developed systematically from these procedures. See figure 2.7.
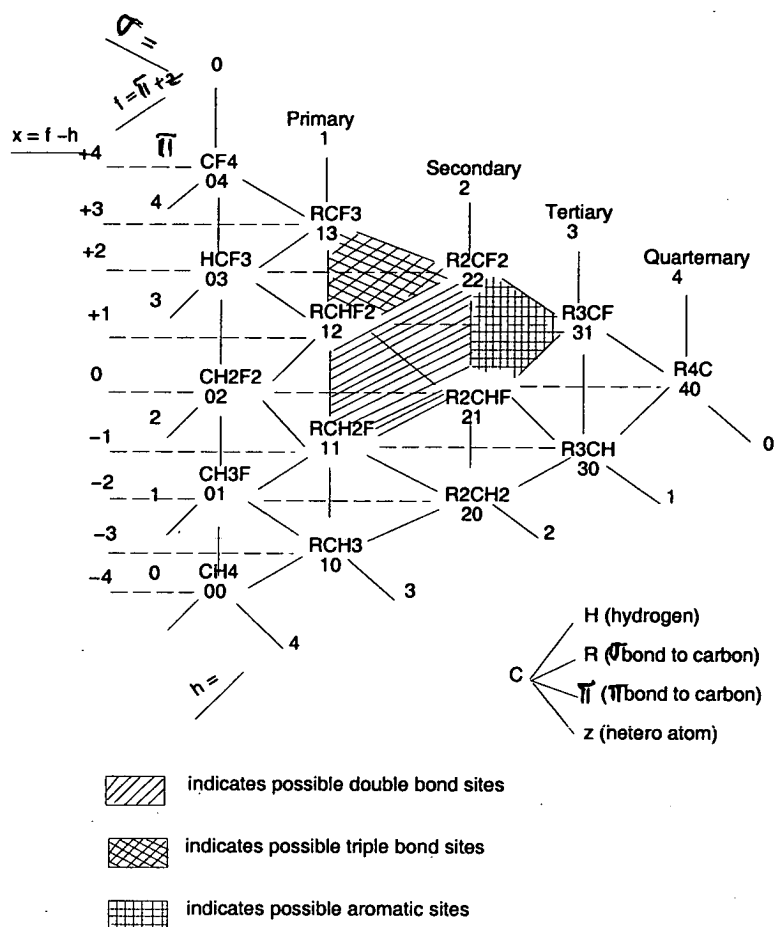
Figure 2.7: Character triangle for carbon sites and interconversions

Direct associative method involves structural subunits to be transformed into a target molecule using standard reactions. The works categorized in this method among others are REACT by Govind and Powers[29], LHASA and SECS both by Wipke[28]. REACT program is a result of a study on the computerization of the representation of molecules succeeded by the generation and evaluation of all possible reaction paths. The purpose of the program is to achieve exhaustive solution of problems with enormous possibilities such as finding starting materials to produce petrochemicals. It could generate a large number of synthetic route of industrial chemicals, which leads to available starting materials.

The program involves the following concepts :

- Small TARGET molecules.
  The basic petrochemical and fine chemical industries commonly deal with fewer than 20 hetero and carbon atoms.

- Multiple target molecules (reaction network).
  The chemical industry is a network of reactions fed by three to five basic materials

and producing hundreds of target molecules. The paths of each target molecule interact with each other by sharing raw materials and by products.

- Stoichiometry must be known in detail, because of its significant impact in the reaction.

- Yield.
  Yield is the fraction of the limiting reagent which is transformed into the desired target molecule must be known.

- By-products
  The amount of by product is a necessary information.

- Impurity reactions must be known due to their major impact in pollution and product quality.

- Reaction conditions must be known including phase, solvents, catalysts, temperature, pressure, concentration, mixing etc.

A molecule is represented by a connection table (CT) defining the atom or group or bond with certain single code number. For examples, single bond is represented by '1', double bond is written as '2' and so on. The use of the single code number provides a way of storing information about the structure, which can then be called from subroutines in the program. Each transformation in the database is represented by its relevant substructure which participate in the reaction. The change matrix is not merely an algebraic difference between the connection table of the reactant and product substructures, but also represents the mechanistic changes that occur in the reaction. Each transformation has checks and contains side products and side reactants that are evolved or required in the laboratory. These information are important for economic consideration. The database also contains normal condition under which the reaction can take place.

The program works in the following manner :

1. Molecule perception
   The process of perception begins with the input of the target molecule which is simply typed in from the keyboard.

2. Transform selection
   It consists of three steps i.e. the matching of the transform substructure with the substructures of target molecule, examining the atoms of the substructure and those adjacent to it and deciding whether the transformation can be expected to be successful in a particular situation.

3. Strategy of transform application
   Large synthesis tree is obtained because of repetitive application and generating many reaction steps. The strategy employs to avoid this condition is to classify each functional group into one of three classes, to allow the pattern matching routine to make one pseudomatch of the functional group and to apply secondary checks and lastly to use blocking target to reduce the reaction steps.

4. Evaluation of reaction paths

   Problems encounter during the evaluation of the reaction paths are yield pre-
   diction normally introduces error due to insuffient kinetic data and problems of
   separation and safety measures.

Figure 2.8 shows the connection table of some simple molecules and its transformation.

MOLECULE   CONNECTION TABLE   LINEAR LIST

OH

C=C–C–C=O

```
4 2 0 0 0
2 4 1 0 0        420004100421608
0 1 4 2 1
0 0 2 6 0
0 0 1 0 8
```

O

C=C–O–C=C

```
4 2 0 0 0 0
2 4 1 0 0 0      4200004100061004216 04
0 1 6 1 0 0
0 0 1 4 2 1
0 0 0 2 6 0
0 0 0 1 0 4
```

Examples of simple molecule representation

C–N–C=O
```
4 1 0 0
1 5 1 0
0 1 4 2
0 0 2 6
```
Product substructure

Change matrix
```
0 –1  1  0
–1 –5 –1  0
 1 –1  0  0
 0  0  0  0
```

C–C=O
```
4 0 1 0
0 0 0 0
1 0 4 2
0 0 2 6
```
Reactant substructure

Reaction representation by their product substructure and
change matrix.
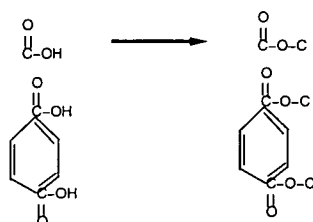
Example of multiple matches of a hydrolysis transform
to Pthallic Acid.

Figure 2.8: The examples of molecule representation and change matrices

The program has been implemented to synthesize several examples such as Phtallic
Acid, Malonic Ester and Methyl Crysanthemate. This work could be extended to
improve the evaluation strategy based on a few simple rules for bondset selection.
The bondset selection is based on symmetry considerations and convergent synthesis,
the use of empirical estimates of reaction yield and the use of linear free energy
relationship to estimate the rate constants.

REACT attempts to cover the complicated structure of the organic molecules and
their reaction paths. The program could recognize and access 29 functional groups

during checks procedures. However the performance of the program has not been tested for larger number of options.

According to Nishida, the Logic Centred method can perform an exhaustive search and provides an opportunity for the creation of really novel reaction paths. On the other hand, the Direct Association method limits the opportunities within the scope of 'known' chemistry. Nishida also suggested the incorporation of the process aspects in the efficient initial screening of the selection of reaction paths such as heat of reaction, the change of free energy and the required temperature and pressure. Aspects related to the economics of the processing systems such as fixed capital and operating cost must also be known. The direction of the work should be focused on the development of working heuristics, although this cannot be achieved in the near future.

Generation of computer based reaction path using Boolean algebra and rate equation in the thermal cracking of normal and branched paraffins has been brought up by Clymans and Froment[30]. In this work, Boolean matrix operation is used to represent the complexity of the hydrocarbon pyrolysis in which only carbon to carbon and carbon to hydrogen bonds are involved. The thermal cracking of hydrocarbons proceeds through a complex reaction network, involving many components including intermediate, final, radical and molecular structures. The number of the components can be large when the feed involves a complex mixture such as naphta or gas oil containing 200 or 300 hydrocarbons. Therefore, the primary reaction mechanisms and the calculation of the coefficients is a complicated and time consuming task. A procedure concerning a binary relation matrix is developed to generate reaction paths and the corresponding rate equations.

Under pyrolytic conditions, hydrocarbons disappear through initiation and H-abstraction, that is the reaction leading to the formation of R_μ^o and R_β^o. R_μ^o are large radicals with carbon number exceeding four, which only disappear through decomposition and isomerization reactions. R_β^o are small chain propagating radicals. The rate of disappearance of 3-methylheptane due to the hydrogen-abstraction by R_β^o and the rate of formation of $R_\beta H$ is equal to :

$$r_{[3-Me-C_7H_{16}]} = r_{R_\beta^o} = r_{R_\beta H} = \left(\sum_i k_{Ab_i}\right)[3 - Me - C_7H_{16}][R_\beta^o]$$

The rate expression for the whole R_μ^o radicals forming due to the H-abstractions is as follows :

$$r_{R_{\mu_i}^o} =$$
$$k_{Ab_i}[3 - Me - C_7H_{16}][R_\beta^o] + \sum_i^{j\neq1}(k_{Is,ji}[R_{\mu j}^o]) - \left(\left(\sum_i^{j\neq1} k_{Is,ij}\right) + \left(\sum_k k_{D_{ik}}\right)\right)[R_{\mu j}^o]$$

In the quasi-steady state, the rates of formation of R_μ^o radicals reduce to linear algebraic equations which can be written as :

$$R_{\mu_i}^o = A_i[3 - Me - C_7H_{16}][R_\beta^o]$$

where A_i is the ratio of sums and products of rate coefficient, temperature dependence but does not obey Arrhenius equation. k_{Ab} is the rate of coefficients of the hydrogen abstraction of the respective atoms, k_D is the rate of decomposition and k_{Is} is the rate of intramolecular isomerization.

The R_μ^o radicals disappear through decomposition and isomerization which leads to olefin, R_β^o and other R_μ^o radicals. The reaction path is developed until a relatively stable olefin and R_β^o radicals are achieved.

For computer implementation, the isoparaffin, 3-methyl-heptane is represented by matrix $\mathbf{M}$ where the C-C bond is denoted by 1. See Figure 2.9. All possible β position of radicals is produced by the square of the Boolean matrix, $(\mathbf{M}^2)$. The fourth power of $\mathbf{M}$, $\mathbf{M}^4$, contains all the possible 1,5 isomerizations. In the next stage all possible ways of decomposition are considered one by one resulting in matrix $\mathbf{M}'$, where the rupture is considered by the non-zero element that is between the second and third in matrix $\mathbf{M}'$. Matrix $\mathbf{M}'$ is divided into two matrices, $\mathbf{O}$ and $\mathbf{R}$. The network is passed through a sequence as shown in Figure 2.9.

The above procedures are exhaustive and the method is straightforward in its application to hydrocarbons. However, the implementation might be limited for it requires certain chemical bonds in its implementation.

In the work on automation of molecular representation, molecules are represented in the form of matrices where the diagrammatical nature of chemical compounds can be captured. The matrices contain bond connections and the number of atoms so called connection table. Transformation of molecules is performed by applying matrix operator having corresponding entries. In these attempts, methodology for automation requires the formulation of chemical compounds into matrices.

2.5.2   Languages for Chemical Reactions

Computational language for reaction and molecular representation has received considerable attention. The objective is to provide a generic computer language that allows flexibility in the generation of the types of molecules and reaction. This is due to the procedures of process design involving complex reaction systems and thus requires complex model. Some recent development on the basic ideas for automated generation using systematical approach refer to the modelling elements developed by Nagel & Stephanopoulos and Prickett & Mavrovouniotis[24, 32]. The modeling elements which are the building block of the language for chemical reaction consist of perception of molecules and reaction network generation. Nagel called their method as Language for Chemical Reasoning (LCR), while Prickett called it Reaction Description Language (RDL). Both languages have slightly different basic modeling elements to represent declarative knowledge about molecules, reactions and pathways. However, in establishing the meaning of the molecules and reaction representation, both languages have similar approach that is by constructing a semantic relationship which is a syntax for chemically reacting systems.

```
                1 2 3 4 5 6 7 8              1 2 3 4 5 6 7 8              1 2 3 4 5 6 7 8
             1 [0 1 0 0 0 0 0 0]          1 [1 0 1 0 0 0 0 0]          1 [1 0 0 0 1 0 0 0]
             2 [1 0 1 0 0 0 0 0]          2 [0 1 0 1 0 0 0 1]          2 [0 1 0 1 0 1 0 1]
             3 [0 1 0 1 0 0 0 1]          3 [1 0 1 0 1 0 0 0]          3 [0 0 1 0 0 0 1 0]
       M =   4 [0 0 1 0 1 0 0 0]   M^2=   4 [0 1 0 1 0 1 0 1]   M^4 =  4 [0 1 0 1 0 0 0 1]
             5 [0 0 0 1 0 1 0 0]          5 [0 0 1 0 1 0 1 0]          5 [1 0 0 0 1 0 0 0]
             6 [0 0 0 0 1 0 1 0]          6 [0 0 0 1 0 1 0 0]          6 [0 1 0 0 0 1 0 1]
             7 [0 0 0 0 0 1 0 0]          7 [0 0 0 0 1 0 1 0]          7 [0 0 1 0 0 0 1 0]
             8 [0 0 1 0 0 0 0 0]          8 [0 1 0 1 0 0 0 1]          8 [0 1 0 1 0 1 0 1]
```

```
                              1 2 3 4 5 6 7 8
                           1 [0 1|0 0 0 0 0 0]
                           2 [1 0|0 0 0 0 0 0]
  Matrix 'O'              3 [0 0|0 1 0 0 0 1]
                    M' =  4 [0 0|1 0 1 0 0 0]       Matrix 'R'
                          .5 [0 0|0 1 0 1 0 0]
                           6 [0 0|0 0 1 0 1 0]
                           7 [0 0|0 0 0 1 0 0]
                           8 [0 0|1 0 0 0 0 0]
```

The reaction sequence :

Figure 2.9: Boolean matrix representation of component and the reaction path

Nagel divides the modeling elements into the following definitions[25] :

1. Modeling elements defining chemical structures

2. Modeling elements defining chemical behaviour related to atom's electronic configuration

3. Modeling elements for reactions and pathways

4. Modeling elements to describe quantitative relationships

In defining chemical structures, Nagel uses a graph theoritic representation of molecular structures where nodes are atoms and edges are bonds. There are 3 modeling elements to describe these and their relations and thus describing the structures. Each modeling element is treated as an object and implemented as a 'class' in an object oriented programming environment. They consist of modeling element for atom, modeling

element for bond and modeling element for atom-bond-configuration. Modeling element for atom comprises attributes of atoms describing atomic characteristics such as *identifier, type, formal-charge, oxidation-state* and so on. This category also consists of atom methods which describe the methods operating on the class atom, such as *compute-hybridization* and *compute-formal-charge*. Since atoms are connected by bonds, each bond must be associated with structures and thus modeling element for bonds is devised. There are bond attributes consist of characters specific to bonds such as *strength, length, type* and *atoms*; bond methods consist of *find-bond-chains, cleave-bond, create-bond* and so on; and bond selectors consist of *alpha-bonds, beta-bonds, terminal-bonds* and so forth. In modeling element for atom-bond-configuration, *empirical-formula, molecular-weight, charge, atoms* and *bonds* become attributes; and atom-bond-configuration methods consist of *make-bonds-from-connectivity-list, setup-atom-bond-graph-descriptor* and so on.

Modeling elements defining chemical behaviour uses the following classes :

- chemical-behaviour which characterizes chemical reactivity

- reaction-environment such as temperature and pressure

- ab-initio-operator for transformation caused by bond cleavage, bond formation and electron distribution

- composite-operator which contains users' specifications and mechanistic operations such as rate constant, enthalpy consideration and free-energy requirements are employed to transform the initial species into products

Modeling elements for reaction and pathways consists of 'reaction' and 'context'. Reaction contains information about the species determining which are the reactants and which are the products. Context is a consistent set of assumptions that characterize a species behaviour or structural character. It is useful when the species can exist in several forms such as resonance structures, or modify pathway without reinitializing the entire system.

The subclass hierarchy of atom bonds and chemical behaviour are depicted in the following figures.
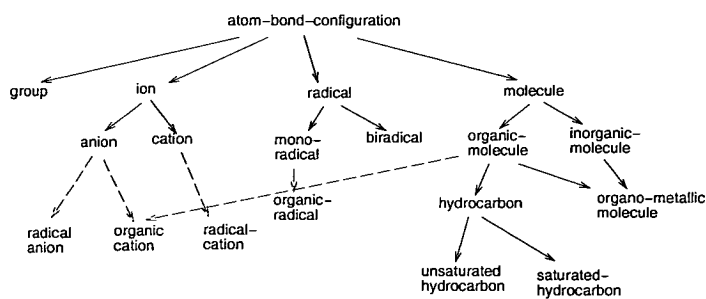
Figure 2.10: Hierarchy of atom bond configuration subclasses
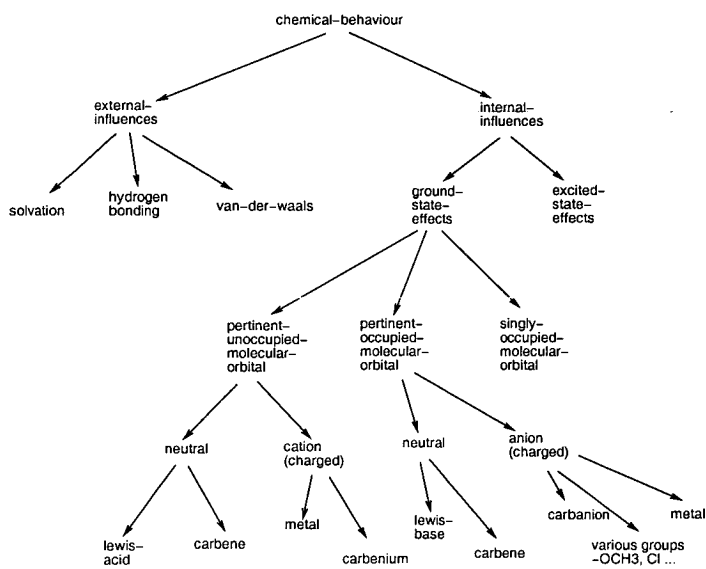
Figure 2.11: Hierarchy of chemical behaviour subclasses

To gain the meaning of all the modeling elements, semantic relations are established to link the elements. The semantic relations also distinguish how different objects correspond to each other. For example *is-attribute-of*, this relationship enables the association of an object as an attribute to another object. The semantic declaration can be something like :

<div align="center">hydrogen-atoms is-attribute-of hydrocarbon</div>

Other relations are : *is-a, is-a-member-of, is-composed-of, is-attached-to* and so on.

In building the syntax of LCR, Nagel uses 'meta-language' which is special language used to describe other languages. He develops the syntax based on Backus-Naur Form (BNF). BNF is a formal method developed by computer scientist for the precise syntactic description of computer languages. The following example shows the syntax of the language used in his work to define the subclass. The first line is the intended definition for variable K_{ai}. The rests are the dependent variables which define each object.

1. $< K_{ai} > ::= < K_{ai} - \text{operator} > < K_{ai} - \text{input} > < K_{ai} - \text{enabling} - \text{cond} > < \text{output} >$
2. $< K_{ai} \text{operator} > ::=$ Bond Formation|Bond Cleavage|Ionization|SingleElectron Transfer|ElectronExcitation|ElectronDecay
3. $< K_{ai} - \text{input} > ::= \{[< \text{reaction} - \text{center} >]^{+}\}$
4. $< \text{reaction} - \text{center} > ::= \{[< \text{atom} >]^{+}\}$
5. $< K_{ai} - \text{enabling} - \text{cond} > ::= \{[< K_{ai} - \text{condition} >]^{+}\}$
4. $< K_{ai} - \text{condition} > ::= \{[\text{physicochemical} - \text{requirements}]^{+}\}$
4. $< \text{physical} - \text{requirements} > ::= (\text{IS} - \text{ABSTRACTED} - \text{BY} < \text{physicochemical} - \text{requirements} >)$

Meaning of symbols :
    ::=   Is defined as
    []   Encloses optional unit
    <>   Unit that is described separately
    {}   Indicates mandatory choice
    ...   Indicates repetition of syntactic signs
    | Separator for alternatives
    +   What the braces enclose may appear any non-zero number of times

The method is illustrated using pathway generation for the oxidation of butane employing free radical chemistry. The results are presented in Figure 2.12 showing 3 different 'contexts'. Each 'context' contains molecular structures, reactions and pathways. These 'contexts' can be linked together to demonstrate the whole representation of butane oxidation.
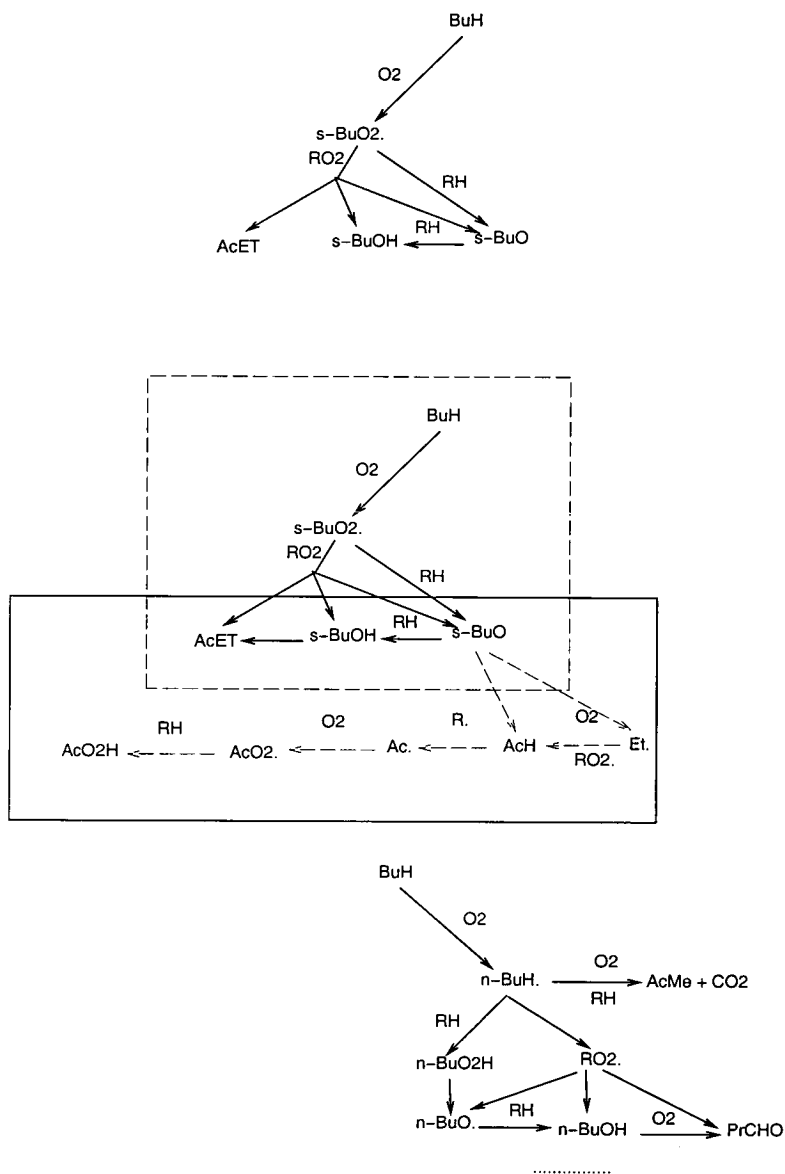
Figure 2.12: Three distinct abstraction in describing the oxidation of butane

LCR is implemented on reaction-based analysis for hazard identification (Nagel and Stephanopoulos)[24]. They proposed inductive and deductive reasonings to generate all potential hazardous events at the top level of design process. The inductive reasoning procedures are bottom up in manner which deal with the operation of a set of chemicals to create many alternative reaction pathways. The deductive reasonings are operated in a top down manner with goal directed which means to eliminate hazards from the knowledge of the plant and its operating conditions.

This predictive hazard analysis to identify the underlying root may overcome the weaknesses of the traditional intrinsic or extrinsic method. Both traditional methods do not have complete identification of hazards because the nature of their approaches is based on stand alone presumption. For examples, the use of just the underlying assumptions on operational modes, or phase equilibria and other physical properties, or simplications, or missing relationship, or the scope of the task. The approach used in Nagel's method focusses on rich representation of knowledge on hazard identification and techniques. Since physicochemical reaction plays the main role in top level hazardous event, every factors determining the initiation of the reaction must be stipulated. These factors include chemical type, chemical reactivity and physical properties. So, the procedures of the hazard identification involve the exploration of reactions leading to potential releases of mass and energy.

Beside LCR, this task also employs MODEL.LA (Modelling Language) ie. modelling language to describe processing systems and their unit operations and behaviour, and to encapsulate the design decisions and operating conditions associated with any specific plant. The inclusion of unit operation modeling allow multilevel description of processes, reactions and material with internal consistency use in the automatic identification of hazards. Hence, different perspectives of the process, reactions and materials such as structural, topological and physicochemical relationships can be investigated independently. However, the review is focused on reaction path generation during hazard identification.

The hazard identification from the set of chemical reactions is demonstrated through the catalytic aniline production from nitrobenzene and hydrogen. The procedure GLOBAL-HAZARD-IDENTIFICATION transforms the reactor into a single terminal process node. The identification of hazards within this node is carried out by applying the procedure IDENTIFY-POTENTIAL-HAZARD. It provides the preconditions associated with each reaction generated by the procedure, FIND-ALL-PATHWAYS. This set contains the known chemical species, i.e. CSS={*nitrobenzene, hydrogen, Raney nickel,* and *phenol*}. Therefore :

$$(\text{FIND-ALL-PATHWAYS } :substrates \text{ CSS } :operators \text{ } K_{hydrogenation})$$

Key reactions identified by the procedure, FIND-ALL-PATHWAYS, are :

$$C_6H_5 - NO_2 + H_2 \rightarrow C_6H_5 - NO + H_2O$$
$$C_6H_5 - NO + H_2 \rightarrow C_6H_5 - NHOH$$
$$C_6H_5 - NHOH + H_2 \rightarrow C_6H_5 - NH_2 + H_2O$$

The overall net reaction is :

$$C_6H_5 - NO_2 + 3H_2 \rightarrow C_6H_5 - NH_2 + 2H_2O$$
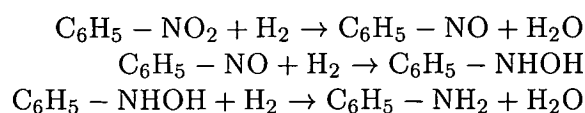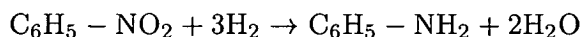
This knowledge allows the explanation of the decomposition temperature of $C_6H_5 - NO_2$, the disproportionation temperature of C_6H_5-NHOH and the preconditions for the exothermic formation of such products as ozobenzene and diazobenzene. Potential reactions of nitrobenzene emanate from this procedures are as follows :

$$C_6H_5NO_2 + H_2 \rightarrow C_6H_5NO + H_2O$$
$$C_6H_5NO + H_2 \rightarrow C_6H_5NHOH$$
$$C_6H_5NHOH + H_2 \rightarrow C_6H_5NH_2 + H_2O$$
$$C_6H_5NHOH + C_6H_5NO \rightarrow C_6H_5NH_2 + C_6H_5NO_2$$
$$C_6H_5NHOH \rightarrow C_6H_5N_2$$
$$\rightarrow (C_6H_5)_2N_2$$
$$C_6H_5NO_2 \rightarrow decomposition\ products$$
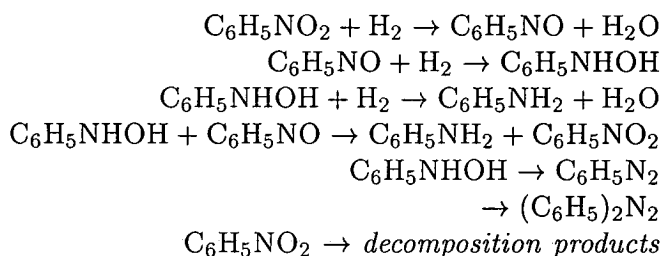
Some of the paths could lead to a hazard, eg. releasing large amounts of energy over a short period of time. By focusing the representation on the thermodynamic state description of the process, the identification of pathways leading to a potential hazards in the most efficient manner can be facilitated, and thus the mapping of the equipment state space (the process flowsheet) to a thermodynamic state space provided that the trajectory of the thermodynamic state is known.

RDL employs strategies which are slightly different from LCR in building up the language. This method is developed considering that the ordinary lump models that useful for determining equipment sizes cannot meet the current challenges in chemical reaction generation. As Mavrovouniotis[31] points out that the design and operation of chemical processes have been faced with increasing competitive and stricter specifications coming from product quality requirements, environmental and other regulations. Therefore the challenges must be met with manipulations in the changing rates in detailed chemical reaction network and detailed molecular transformations, including complexity description and modelling.

The method comprises perception of molecules, description of reactions and network generation. The perception of molecules defining chemical structures involves unique molecular representation so that they can be manipulated by other modules. The tasks also deal with the translation of initial chemical structures of a compound into internal machine language. In this work, input representation of molecules is based on the SMILES codes[34] which is believed to be the most informative and flexible communication between human and machine for chemical notation. In SMILES, the molecule is represented in a simple text string so called line notation of a compound. SMILES has been used by Prickett and co workers[32] in their work on the construction of complex reaction systems with slight modification to meet their need. The conventions involve symbols of atoms, bonds and chains. The following lists show some of the symbols used in representing chemical molecules in line notation.

- standard symbol for atoms, such as C,H,S ..etc

- bonds are denoted as sb, db, tb, arb for single, double, triple and aromatic bonds

- branch chain is enclosed in parenthesis

- cyclic is symbolized by two "R"s (with apostrophe) enclosing the carbon chain

Single bond and hydrogens do not have to be included in the structure. The following lists show the representation of several components.

- c1 c c : for propyl cation
  The numbering denotes primary propyl cation

- c c (c) db c c c : for 2-methyl-2-pentene
  Branch chain is enclosed in parentheses and placed after the second carbon atom. Double bond must be inserted in between the second and third carbon atoms.

- c "R1" c c c c "R1" for cyclo hexane
  The numbering in "R" denotes the edge of the connection of the cyclic component.

In the course of reaction network generation, duplication of compounds may occur. To enable a unique description of a compound, canonicalization is necessary to rule out the equivalence of two or more molecules. Canonicalization yields a standard and unique numbering of the atoms of a molecule. The canonicalization algorithm involves iterative refinement of a partitioning of the atoms into classes and encodes the indices used in the partitioning as ordered lists. This process creates the topology of the atoms, and therefore if a structure contains an heteroatom which is less prevalent than carbon atom, then the first symbol in the canonical form is the heteroatom. If the equivalent of this compound is checked with paraffin, then the difference will be detected.

Description of reactions includes representation of reactions and commands. Representation of reactions is generic that is an abstract description of an entire family of ordinary reactions. For example, dehydrogenation of alkane results in alkylation. Any compound belongs to alkane undergoing similar treatment would return similar product. The number of reactions generated is restricted by 'requirement' rules or 'forbidden' rules, indicating whether a reaction should be applied to a specific site. The commands used in reactions imitate the natural behaviour of reactions.

The generic reactions are then compiled in network generator. The algorithm of the network generator includes descriptors of the initial species and reactions.

The method presented here is also implemented in a complex reaction system which usually involves known types of reactions, but unknown specific reactions (Mavrovouniotis and Bonvin[31]). A general type of reactions specifies what molecular substructures or categories of compounds the reaction applies to and how it alters the structure of the compounds. A specific reaction, on the other hand, involves individual chemical compounds with a specific stoichiometry. Figure 2.13 shows the removal of a hydride as in acid catalyst for Fluidized Cracking Catalytic (FCC) with formation of a cation.

a. Hydride abstraction from a neutral alkane, where A+ represents
the catalyst site that picks up the hydride.

b. Hydride shift, leading to isomerization of an ion.

c. Scission of an ion to form an alkane and another ion.
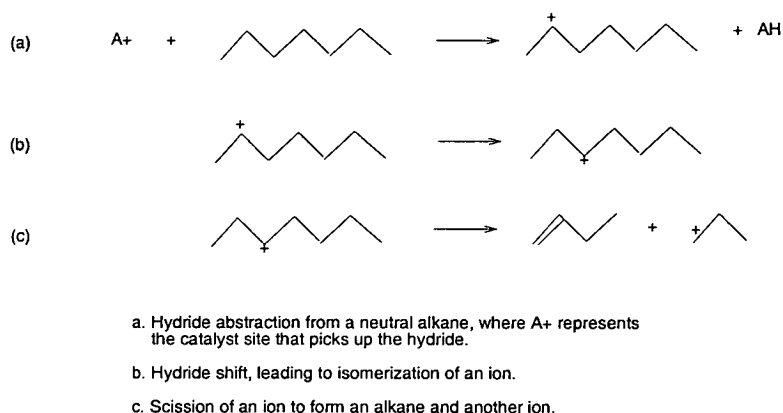
Figure 2.13: Examples of three reaction types

As for example, reaction 'a' above is described in the following language :

    (Require hydrocarbon molecule)
    (Require neutral molecule)
    (Label C1 (Find carbon))
    (Forbid (Find-exactly 3 hydrogens attached-to C1))
    (Label H1 (Find hydrogen attached-to C1))
    (Disconnect C1 H1)
    (Add-charge C1)
    (Set number-of-reactions (Symmetry-number H1))

The last command (Set number-of-reactions (Symmetry-number H1)) is intended to reduce complexity by treating all equivalent atoms collectively.

In a methyl group, the three hydrogens are equivalent; the procedure will examine only one and will store the symmetry number 3 in the generated reaction to account for the multiplicity. The line (Forbid (Find-exactly 3 hydrogens attached-to C1)) is intended to exclude primary ions, on the assumption that they are not favored thermodynamically. Similar procedures are applied to reactions 'b' and 'c'. The results show that the total number of reactions constructed in this case is 441. However, despite the high complexity, this system does not include all possible isomers and reactions in this carbon-number range. There are many more than 29 C7 compounds (even restricted to at most 1 charge and 1 double bond), but most of them are simply not accessible from the starting materials and the 5 reaction types of this example.

Both LCR and RDL adopt the fundamental concept of the chemistry to generate rules and models for the chemical structures and their behaviour. They provide a comprehensive methodology and procedures for automatic chemical reactions. This is shown by the results of the case studies which generate all possible pathways, enabling conditions, competing reactions as well as generation steps. The methods do not only deal with the synthesis of reaction paths, but also towards the generation of any chemical reaction. However, the consequencies are, large size of computer codes will be required

to accommodate every single chemical reaction and thus its pathways.

2.6   Conclusions from Literature Review

The development of tools for reaction path synthesis began with the formulation of the behaviour of reaction clusters using simple graphical approach. The effort has provided insight into the behaviour of reaction clusters which may lead to the discovery of new clusters. With an increased number of species to consider, algebraic formulation incorporating stoichiometric and thermodynamic constraints was introduced to broaden the selection scope. This was also coupled with economic considerations so as the reaction selection is favourable from commercial aspect. Further developments show that the procedures devised are chiefly driven by the type of the problem being investigated. Using environmental impact minimization as the objective, synthesis of reaction paths is carried out to produce commercially important but environmentally benign processes. Synthesis on biochemical process routes has also been developed based on natural behaviour of bioreactions.

In recent years, reaction path synthesis has been influenced by the developments in computing technology. Originally, computational efforts in chemistry centred around acquiring, storing and retrieving information from a database. The need for automatic reaction generation and structural transformation has brought about techniques on molecular representation which has become crucial since it must be able to provide a unique description of molecules. At this stage, researchers used matrices and rigorous mathematical model to describe molecules and reactions. Later on, concepts originated in computer science and artificial intelligence such as qualitative reasonings have enabled descriptive representation of molecules and reactions. Its implementation in reaction pathway synthesis has led to the development of languages for chemical reactions. These languages are developed to model complex reaction systems and to be capable of describing reaction networks.

The use of reaction paths in the hierarchical approach of conceptual process design shows that the selection and connectivity of process units are dominated by the reaction chemistry. This suggests that reaction path synthesis is important, and it is necessary to have a few best alternatives be determined at the earliest level.

The tools that have been developed in this area are aimed at generating reaction pathways or reaction networks focussing on thorough assessments of major reactions. Undesired reactions are taken into consideration as minor objects which have to be discarded. However, the occurence of these other reactions are unavoidable, and the accumulation of minor species may lead to problems in the process units. Therefore, a procedure to identify the generation of minor species is deemed necessary and the development is explained in Chapter 3.

Chapter 3

Method

For the purpose of investigating side reactions in a chemical process, procedures capable of generating all possibilities are required. The procedures must be able to accommodate both structural representation and reaction generation automatically. Heuristic based tools such as graphical representation could be cumbersome to deal with a large problem. Beside non-automatic features, these tools are not provided with molecular representation. Methods presented in developing chemical language are perhaps potentially useful, but at the same time they are too detailed for our application. It is proposed that a systematic approach using group contributions be applied. The technique can be used not only for molecular representation but also to determine types of reaction involved and to generate species. Group contributions are also used to determine molecular properties. Our aim will be to avoid the need to represent rigorous chemistry. The heuristic but systematic approach used in the present work is described in this chapter.

We require the following facilities which have also been used by other workers[28, 25, 32]. The definitions presented below are adapted from the definitions given in Nagel's modeling languages[25].

1. A means of defining chemical structures
   These are associated with structural formulae, functional groups, atoms and bonds.

2. Definition of reactive behaviour of chemicals
   The reactive behaviour of chemicals is determined by functional groups which means the tendency of the atom bonds to cleave and form radicals.

3. Definition of reactions and pathways
   Reactions contain information about the species determining the reactants and the products. Pathways are the routes taken to generate certain chemicals.

The approach is discussed in two subsections, Representation of Structure and Method respectively.

3.1 Representation of Structure

Models for chemical structures require the capability to represent a compound uniquely. The representation must also be conveniently manipulated. In the present work, molecules are represented in linear notation as standard ASCII characters, somewhat similar to SMILES[34], a system originally developed for chemists to access chemical databases. In SMILES, hydrogen atoms belonging to carbon atoms are suppressed. The structure is constructed in two dimensional form so as establishing a skeleton of carbon atoms. As atom bonds are also specified, the method provides a unique representation of chemical compounds. Examples are CC for ethane, C=C for ethylene and CCN(CC)CC for triethylamine. The compactness of the representation is convenient as a descriptive language, but requires further interpretation to extract precise molecular information. For this reason, we did not use SMILES notation.

As it is required to estimate chemical properties based on group contributions, molecules are built up directly from functional groups rather than as atoms to avoid additional recoding. As in the above examples, ethane will be written by embedding two CH3's, that is CH3CH3, ethylene is CH2:CH2: and triethylamine becomes CH3CH2[CH3CH2]NCH2CH3. Notation for branches is created in a different way, with the ethyl branch is enclosed in square brackets. The group contribution method adopted is the Lydersen technique as improved by Joback[39]. See Appendix A. Details of the notation are given below.

Conventions used in this work are as follows :

- standard symbol for atoms, such as C,H,S,Cl,Br,F ..etc

- bonds are denoted with no symbol for single, ' :' for double, '#' for triple

- branch chains are enclosed in square brackets

- cyclic chains are indicated by lower case letters enclosed in curly brackets

- normal groups are written in upper case with bonds denoted such as CH3, CH2, COOH, CHO, C6H4, CH2:, CH#, etc.

Species are built up from the functional groups used by Joback[39]. The Joback group contribution technique is selected due to the following factors :

- Joback technique was developed based on the Lydersen technique which was found to be efficient and successful in estimating critical properties.

- Representation of functional groups in Joback's method is relatively simple and can be used directly to build chemical structures by embedding groups together.

- The application of free radicals to generate new species which frequently requires fragmentation of molecules. These molecules can be fragmented into Joback functional groups.

In constructing a molecule, the groups are arranged according to the typical structure of the molecule as far as possible. CH3 group should be located at the edge of the string, indicating that it has one unpaired electron. Similarly, CH2 should be put in the middle denoting two unpaired electrons. Functional groups such as aldehyde (CHO), acid (COOH), alcohol (OH) etc, should be written at the end of the string. Components having a double bond or a triple bond, are indicated by two groups having the respective bond. An aromatic ring is shown by using 'C6H' followed by the number of hydrogen atoms, e.g. phenyl is written as C6H5, xylyl as C6H4 and so forth.

Branch chains, rings and cyclics can be nested. Groups which are positioned adjacent to square or cyclic brackets indicate that these groups are the connecting point of the branch chain or the ring. The way the molecules are represented in this task provides a unique molecular structure. The following table (Table 3.1) shows the construction of some particular molecules.

Table 3.1: The construction of components in line notation

CH3CH3	ethane
CH3CH2COOH	propionic acid
CH2:CH2:	ethene
CH3C#CH#	propyne
CH3[CH3]CHCH3	isobutane, the branch chain (methyl branch) is attached to the tertiary carbon 'CH'
CH2 : [CH3[CH3]CH]C : CH2CH3	3(2-methylpropyl),3-butene
{ch2ch2ch2ch2}	cyclobutane
CH2:CH:{chch2ch2}	ethenylcyclopropane
CHCl3	chloroform
CH3CH2COCH3	butanone
CH3CH2CHO	propanal
C6H5{OH}	phenol
CH3C6H4CH3	dimethyl benzene or p-xylene
CHOCHO	ethanedial
CHOCOOH	glyoxylic acid
CH4	methane
C6H6	benzene
H2	hydrogen
CO2	carbondioxide

Database of the group properties consists of molecular weight, boiling point, critical temperature, critical pressure, critical volume, heat capacities, enthalpy and free energy change. The database is divided into two sections, a pure component section and a functional group section. A pure component section represents those which cannot be broken down into groups by the above approach; for example, CH_4, H_2O, H_2S, NH_3, HCl, HBr, H_2, O_2, CO_2, C_6H_6. The functional group section contains all groups used in Joback group contribution method. See Appendix A.

3.2 Method

The purpose of the work is to reveal every possibility of chemical species generation. The approach taken is to regard these as being created in a sequence of consecutive reactions. Reaction proliferation is driven by the creation of species in previous reactions. The problem solving is divided into three main stages:

1. Species and reaction generation
   The generation of possible byproducts

2. Stoichiometric feasibility
   The identification of stoichiometrically feasible reactions leading to byproducts, and elimination of stoichiometrically infeasible byproducts

3. Thermodynamic feasibility
   Screening out those reactions which are thermodynamically unlikely under the proposed reaction conditions.

3.2.1 Species and Reaction Generation

Species generation involves representing the reactive behaviour of chemicals. For this purpose, the concept of free radicals is used because of its existence in a wide variety of reactions, although the term used here is broader than the strictly correct chemical sense. The formation of these radicals depends largely on the reactivity of chemicals corresponding to the class of the components. Component classes correlate with physical properties which have been classified according to the nature and number of atoms in a molecule. These properties are additive, constitutive and colligative dependent on the number of atoms, the arrangement of atoms and the number of molecules respectively. Substances having different atoms have different intermolecular forces and thus determines the attractive and repulsive forces. In organic chemistry, the intermolecular forces determine how molecules fragment. Fragmentation occurs towards the most stable carbonium ion or free radicals, and this also indicates the relative labilities of bonds or the stabilities of the fragments. These fragments consist of functional groups in which the most stable free radicals are aromatics while the least stable relative to aromatics are alcohols. The removal of an atom or a group is therefore largely dependent on the structure, a slight change in the structure can provide different chemical properties[36]. Details on fragmentation patterns are available in Appendix B.

An inference engine embodying simplified rules of chemistry as described above was set up. The different characteristics of each component class are coded in the sets of rules involving all possibilities in the nature of bonds undergoing fission. The inference engine thus determines the behaviour of chemicals and decides the types of reactions involved. As an illustration, below are general mechanisms of radical formation of certain component classes.

1. Alkane

   - Abstraction of hydrogen atom

- Fragmentation of methyl, ethyl, propyl .. etc, or in other words alpha or beta cleavage

2. Alkene

    - Abstraction of hydrogen atom
    - Formation of single bond
    - Fragmentation of alpha and beta bond

3. Arenes

    - Formation of C_6H_5, C_6H_4

4. Alcohols and ketones

    - Alpha cleavage
    - Beta cleavage
    - Alcohol dehydrogenation
    - Alcohol dehydration

5. Aldehydes and acids

    - Beta cleavage

α, β, and γ bonds are the position of carbon atom relative to the position of a double bond or a functional group. The mechanisms work as follows: if a set of reactants consists of an alkane species such as CH_3CH_3, then this species will undergo hydrogen abstraction forming $CH_3\dot{C}H_2$ and $\dot{H}$, and also fragmentation forming a methyl, $\dot{C}H_3$. These radicals originated from a single or more initial components are then combined to form new chemical species.

The new species are generated by combining the radicals. Rules are incorporated while putting the radicals together. Hence, combining radicals is restricted by rules of thumb such as: 'a ketone may not contain an aldehyde group', or 'a structure having two double bonds cannot have two hydroxyl groups'. These rules are incorporated in order to avoid 'unknown' or invalid species being generated. Some 'unknown' species might be considered valid when they cannot be ruled out by thermodynamic screening.

Another way to help eliminate invalid species is by providing the program with rules containing the type of reactions. The rules work to guide the program on generating the right radicals and species. Examples are shown using oxidation reactions for some of chemical species below.

1. Alkene
   Oxidation of alkenes exhibit different results depending on the structure, oxidative reagent and the reaction conditions.

    - Carbon-carbon cleavage at double bond
      $R_1-[R_2] - C{=}C-[R_3]-R_4 \rightarrow R_1-[R_2]-C{=}O + R_3-[R_4]-C{=}O$
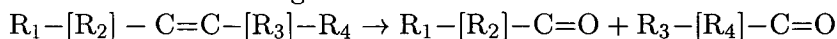
- Addition of hydrogen peroxide elements or hydroxyl ($H_2O + \frac{1}{2} O_2$)
  $R_1-[R_2]-C=C-[R_3]-R_4 \rightarrow R_1-[R_2]-[OH]-C-C-[OH]-[R_3]-R_4$

- Formation of cyclic oxygen compound
  $R_1-[R_2]-C=C-[R_3]-R_4 \rightarrow R_1-[R_2]-\{c-c-o\}-[R_3]-R_4$
  $R_1-[R_2]-C=C-[R_3]-R_4 \rightarrow R_1-[R_2]-\{c-o-o-c-o\}-[R_3]-R_4$

2. Secondary alcohol
   $R-CH-OH-R_1 \rightarrow R-C=O-R_1$
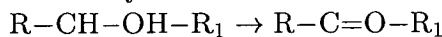
3. Aldehyde
   Formation of carboxylic acid
   $R-CHO \rightarrow R-COOH$
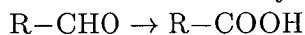
4. Acids
   Formation of CO_2 and H_2O

The process of identifying the reaction types is performed before generating the new species. The generation of radicals should thus follow the way the species might react under certain circumstances. Once the new species are generated, reactions will be constructed from the combination of initial species, as the reactants, and the new species, as the products. The number of products involved in each reaction may be from one to three components. The reactions are screened using stoichiometric and thermodynamic criteria elaborated in more detail in sections 3.2.2 and 3.2.3 respectively.

Figures 3.1 and 3.2 show the algorithm for the generation of species and combining them with each other to generate new molecules. Figure 3.1 shows the radical and species formation. The program starts by identifying the type of reaction followed by identification of the type of molecule so that radicals can be generated according to its class reactivity. The species are formed by combinatorial approach, that is, mapping the radical elements, and is followed by species pruning. Here, the number of species are reduced by eliminating redundancies.

Figure 3.2 shows the algorithm of the species formation in detail. As described above, components are divided into two groups, i.e. pure components and components comprising functional groups. Refer to Section 3.1. For pure components, radicals are likely to form by hydrogen absraction or atom abstraction only. For components comprising functional groups, the length of the chain determines the occurrence of the types of chain cleavages as shown in the above figure.

1. Reaction Identification

1.1 Hydrogenation

1.2 Oxidation

1.3 Alkylation

2. Molecule Identification

1.1. Alkane
   - Abstraction of hydrogen atom
   - Fragmentation of methyl, ethyl, propyl, ...etc

1.2. Alkene
   - Abstraction of hydrogen atom
   - Formation of single bond
   - Fragmentation of beta-bond

1.3. Arenes
   - Formation of C6H5, C6H4

1.4. Alkanols
   - Alpha and beta cleavages
   - Alcohol dehydrogenation and dehydration

1.5. Aldehydes and ketones
   - Alpha cleavage
   - Beta cleavage

3. Combinatorial Radical Reaction

Element mapping

4. Radical Pruning

Eliminate redundancies

5. Molecule Combinatorial Reaction

6. Reaction Pruning

Themodynamic constraint

Figure 3.1: Algorithm of radical and species formation

Component

Pure Component

identification of :

Atom elements
Position of atoms in component

Radical Formation

by means of :

Hydrogen abstraction
Atom abstraction

Functional Group

identification of :

Group elements
Position of groups in component

Radical Formation

by means of :

Hydrogen addition for unsaturated Hydrocarbon

Alkylation of alkane

Hydrogen abstraction from functional group

Alpha–scission

Beta–scission

Gamma–scission

Combinatorial formation of free radicals
generating new molecules/component

Reactions of new molecules

Figure 3.2: Detailed algorithm of species formation

3.2.2   Stoichiometric Feasibility

The second step involves a combinatorial approach to determine reactions that feasibly produce the species that are generated in the first stage. Each reaction consists of species determined as reactants and those as products with variables represent stoichiometric coefficients. By convention, reactant coefficients are given negative value and those of products are positive. The atom balances of reactions generate a set of linear equations subject to the stoichiometric coefficient variables. These build a matrix with the number of coefficient variables as the number of columns and the number of atoms as the number of equations. Hence, the number of equations depends on the number of atoms. The solution is found by a linear equation solver. The detail of the procedures are exemplified below for the chlorination reaction of methane.

$$a \ CH_4 + b \ Cl_2 = c \ CH_3Cl + d \ HCl$$
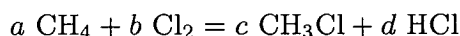
a, b, c and d are the variables of the stoichiometric coefficients to be identified. The coefficients of matrix produced from the reaction with respect to atom C, H and Cl are :

$$
\begin{array}{lllll}
C: & -1 \ a & 0 \ b & +1 \ c & 0 \ d \\
H: & -4 \ a & 0 \ b & +3 \ c & +1 \ d \\
Cl: & 0 \ a & -2 \ b & +1 \ c & +1 \ d
\end{array}
$$

Coefficient values are relative, so assume that a is unity. The values of a are brought to the right hand side of the matrix equation. The atom balance equations are thus :

$$
\begin{array}{ll}
C: & c = 1 \\
H: & 3 \ c + d = 4 \\
Cl: & 2 \ b - c - d = 0
\end{array}
$$

Hence, the matrix would be equal to :

$$
\begin{pmatrix}
0 & 1 & 0 \\
0 & 3 & 1 \\
-2 & 1 & 1
\end{pmatrix}
\begin{pmatrix}
b \\
c \\
d
\end{pmatrix}
=
\begin{pmatrix}
1 \\
4 \\
0
\end{pmatrix}
$$

The linear solver identifies that there is a solution with values of b, c and d of 1. The reaction is considered plausible if :

- A solution exists

- Its values are small whole numbers

- $b = 1$. A value of $b = 2$, although a small integer, would not represent a feasible elementary reaction.

The number of atoms building the number of equations and the number of species building the number of reaction coefficients are not always ideal. There are variations in the combinations of the number of equations and the number of variable coefficients. These can be divided into several categories :

1. The number of atom types equal the number of reaction coefficients
   Oxidation of complex compounds are usually in this category. For example :

$$a \ OHC_6H_4CH{=}CHCOOH \rightarrow b \ OHC_6H_4CH{=}CH_2 + c \ CO_2$$
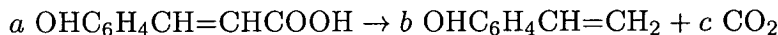
The number of atoms is 3, likewise the number of reaction coefficients. Therefore the coefficient matrix must follow the actual position of a, b and c, while the right hand matrix is manifested as zero. The resulting matrix must look like this :

$$\begin{pmatrix} -9 & 8 & 1 \\ -8 & 8 & 0 \\ -3 & 1 & 2 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix}$$

2. The number of reaction coefficients exceeds the number of atoms

$$a \ OHC_6H_4[OH]CHCH_3 + b \ O_2 = c \ H_2 + d \ OHC_6H_4CH_2OH + e \ CO_2$$
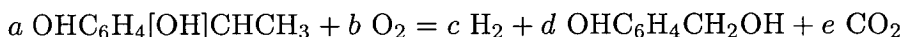
There are 3 atoms and 5 coefficients. Since we have restricted the reactant coefficients to one, then the number of coefficient variables can be reduced by summing up a and b creating a new variable. The new variable is shifted to the right hand side matrix. The rest of the procedure is similar to the chlorination reaction.

3. The number of atoms exceeds the number of coefficients
   This situation is typically a reaction such as the following.

$$a \ CH_2{=}CH{=}CH_2CH_2CHO \rightarrow b \ CH_3CH{=}CHCH_2CHO$$
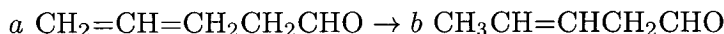
The number of atoms in this example is 3, while the number of coefficients is 2. Since a is assumed to be one, then b must have the value of one for the stoichiometric coefficients to be in balance. Linear equation solver is not applicable if such situation occurs.

The determination of stoichiometric coefficient is coupled with investigation of atom balance to determine feasible stoichiometry and eliminate infeasible reactions.

3.2.3   Thermodynamic Feasibility

Thermodynamic criteria are applied to further test the likelihood of a stoichiometrically feasible reaction. Free energy (ΔG) of the reaction is determined from the free energy change of reactants and products estimated using Joback group contribution method[40].

Free energy is defined by the following equation :

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy changes (ΔH) in a reaction are concerned with the alteration in bond energies obtained by totalling all the bond energies involve in the reactants and products. Negative ΔH refers to exothermic reactions, while positive ΔH denotes endothermic reactions. Entropy changes (ΔS) refer to the randomness of the system for which the less order a system the greater the entropy. A spontaneous reaction will prefer negative enthalpy changes and positive entropy changes. In many cases, entropy has little effect in a spontaneous chemical reaction[37, 38]. See Appendix C for details.

Thermodynamic criteria can indicate whether a process or a reaction occurs, but it cannot indicate the reaction rate and the quantitative description. However, this work does not aim to give an indication as to which the major products are or which the minor ones. The main concern is to obtain a description on the components that might be produced from a given chemical species.

Temperature also plays an important role in the transformation process and has been taken into consideration. The effect of free energy changes as the function of temperature changes is given in the following relation :

$$\frac{d(\Delta G_T^o/T)}{dT} = -\frac{\Delta H}{T^2}$$

The integration of the above equation is shown in Appendix C which shows the correlation of the free energy changes with the enthalpy changes and temperature changes. Therefore, a reaction may not occur at standard condition, but it may have favourable equilibrium condition when the temperature is raised. In this study, free energy changes are calculated at temperatures which are varied in the range of 298 to 1500 K. If a negative free energy change is identified within this range, then the reaction is deemed to be possible.

3.3 Implementation and Visualisation

The algorithm for the complete task consisting of the generation and evaluation steps as discussed above is illustrated in Figure 3.3.

The stages described in section 3.2 above form what we will refer to as a cycle. Series of cycles are created automatically using a build-tree program. The numerical procedures of the cycle are implemented in Fortran 90 while the build-tree program is written in LISP. The purpose of the build-tree program is mainly for user interaction and visualisation of species generation. This program can be used to analyse the extent of the species generation and also to examine the reaction pathways.

For visualisation, species and reactants are treated as nodes and paths respectively as in a graph[41]. See Figure 3.4. The start node is the original starting species, while the goal node is specified according to the level of species expansion. All nodes will be explored to produce descendants of species. In this work, the level of expansion of the tree is set according to the number of species generated or until exhaustive search is reached.
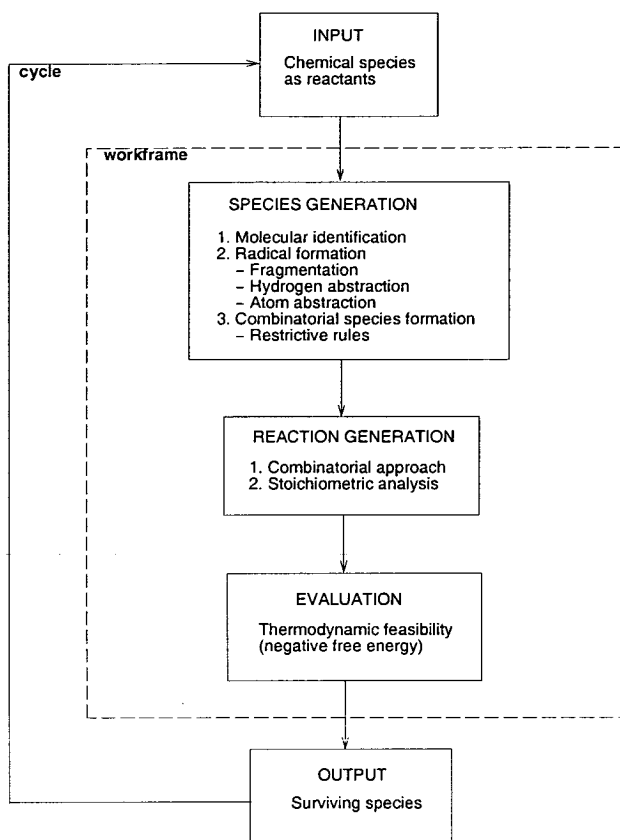
Figure 3.3: Algorithm of automated generation of reaction paths

To indicate each generation task, we define the term *level* which denotes the depth of the expansion. The first level is the cycle contains the starting species, while the next levels are those proceeding from the surviving species of the first level. The procedures are repeated for each surviving species which in turn create a species tree. Ideally, the expansion terminates when there is no new species generated or the number of nodes exceeds a specific value. In the latter case, the limit of the expansion can be set up from the beginning. The expansion is done automatically on a best-first search by default, however breadth-first and depth-first expansions are also available. Interactive mode can be used when there are only necessary nodes to be expanded. The following diagram illustrates the tree with nodes and paths denoting species and reactions respectively.

3.3.1 Programs

There are three separate programs deal with three specific tasks. The objectives of the tasks are :

- To generate chemical species automatically
  This is done by a program called *Generate.*

- To generate chemical reactions from the initial species and the newly generated species
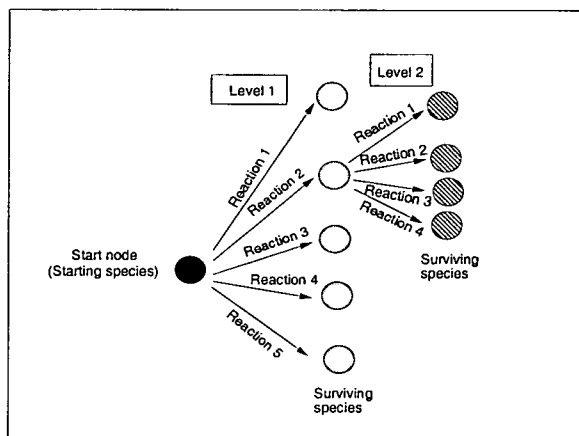
Figure 3.4: Illustration of a tree with starting species, reactions, and surviving nodes

This is accomplished by a program called *React*.

- To evaluate the feasibility of the chemical reactions
  The program is called *Evaluate*.

These programs are the workframe controlled by a build-tree program positioned at the topmost level of the execution process. The build-tree program provides input to the species generator, passes the new products to the reaction generator, and takes output from the evaluator. The output thus become the new input at the next stage. This process creates cycles which develops consecutive reactions within a defined expansion level. The structure of the programs is elaborated in the following sections, with each section is referred by the name of the programs.

Program *Generate*

The program starts by reading the initial species from an input file provided by the users, called *input*. The next input files are generated automatically from the surviving species of the previous levels. The species generator takes the species in the input file and generates radicals.

```
program Generate_Chemical_Species
        read no_reactant
        read reactant(i), i = 1,no_reactant
        call generate_newspecies(no_reactant,reactant)
end program
```

This procedure is followed by generating new components through radical combinations. The results are stored in an output file given *.species* extension to indicate the file

contains species generation data. The name of the output files are given in order of cycles, such as *G868.species* or *G869.species*.

```
subroutine generate_newspecies(no_reactant,reactant)
        call reaction_type(reactant,no_reactant,type)
        call generate_product(no_reactant,reactant,type,newmols,no_newmol)
end subroutine
```

Subroutine *reaction_type* determines the type of reaction that might be involved when given a set of reactants. For example, if the reactants consist of oxygen, then oxidation reaction will occur. Likewise, if the reactants consist of halogens and an alkane, then halogenation will occur. The procedures for radical formation will be chosen as to facilitate oxidation or halogenation reaction respectively.

```
subroutine generate_product(no_reactant,reactant,type,newmols,no_newmol)
        call generate_rad(no_reactant,reactant,type,radicals,no_radicals,
                valence,head,position)
        call product_formation(no_reactant,reactant,type,radicals,no_radicals,
                valence,head,position,newmols,no_newmol)
end subroutine
```

```
subroutine product_formation(no_reactant,reactant,type,radicals,no_radicals,
                valence,head,position,newmols,no_newmol)
        call newmolecule(radicals,no_radicals,valence,head,position,
                newmols,no_newmol)
        call eliminate_redundancies(newmols,no_newmols)
end subroutine
```

Subroutine *check_component_class* contains procedures to determine the type of component. Argument *groupname* passes information on functional groups, which will be classified according to its class. If one of the groups is in the form of 'CO' then a ketone is identified, similarly to 'CHO' for aldehyde, 'COOH' for acid and so on. An alkane is identified by the standard empirical formula of C_nH_{2n+2}, while an alkene is recognized by the presence of double bond.

```
subroutine generate_rad(no_reactant,reactant,type,radicals,no_radicals,
                valence,head,position)
    do counter = 1,no_reactant
        component = reactant(counter)
        call find_group(component,groupname,grouppost,mgroup,comptype)

        if (comptype == group) then
            call group_radical_formation(component,groupname,grouppost,mgroup,
                    radicals,no_radicals,valence,head,position)
        else if (comptype == pure_component) then
            call pure_radical_formation(component,radicals,no_radicals,
                    valence,head,position)
        end if
            call eliminate_redundancies(radicals,no_radicals)
        end do
end subroutine
```

```
subroutine group_radical_formation(component,groupname,grouppost,mgroup,
                radicals,no_radicals,valence,head,position)
    call check_component_class(groupname,mgroup,class)
    if (component == alkane) then
        call rad_formation_alkane(component,groupname,grouppost,radicals,
                mgroup,no_radicals,valence,head,position)
    end if
    if (component == alkene) then
        call rad_formation_alkene(component,groupname,grouppost,radicals,
                mgroup,no_radicals,valence,head,position)
    end if
    if (component == aldehyde) then
        call rad_formation_aldehyde(component,groupname,grouppost,radicals,
                mgroup,no_radicals,valence,head,position)
    end if
... and so on
end subroutine
```

```
subroutine pure_radical_formation(component,radicals,no_radicals,
                    valence,head,position)
        call hydrogen_abstraction(component,radicals,no_radicals,
                    valence,head,position)
        call atom_abstraction(component,radicals,no_radicals,
                    valence,head,position)
end subroutine
```

```
subroutine newmolecule(radicals,no_radicals,valence,head,position,
                    newmols,no_newmol)
        call newmole_onevalence(radicals,no_radicals,valence,head,position,
                    newmols,no_newmol)
        call newmole_twovalence(radicals,no_radicals,valence,head,position,
                    newmols,no_newmol)
        call add_hydrogen(radicals,no_radicals,valence,head,position,
                    newmols,no_newmol)
        call add_hydrates(radicals,no_radicals,valence,head,position,
                    newmols,no_newmol)
... and so on
end subroutine
```

The radical structure is identified by a *valence* number and the radical position. *Valence* denotes the number of sites for possible attachments or in other words unpaired electron. The *valence* is given a minus sign so as to indicate the loss of atoms and thus capable of receiving other atoms or radicals. The radicals that can be combined must have the same *valence* number individually or in total. If the *valence* of a radical equals 1, the number of other radicals that can be attached to the radical is one. If the *valence* equals 2, then the number of other radicals that can be combined are two for radicals with *valence* 1, or one for radicals with *valence* 2. *Radical positions* denote the location of group from which atoms have been removed and thus define the position of the site. *Head position* defines logical options, *head position* is true if the radical group is located at the left hand side of the radical, otherwise it is false.

Program *React*

Reaction generator reads the reactants and the products from the output file of the species generator and establishes reactions having feasible stoichiometric coefficients. The results are written into an output file called *filename.reaction*. The structure of the program is shown below.

```
program Generate_Chemical_Reactions
        read no_reactants,reactants,no_products,products
        generate_reaction(no_reactants,reactants,no_products,products,reaction)
end program
```

```
subroutine generate_reaction(no_reactants,reactants,no_products,products,reaction)
        call set_reaction(no_reactants,reactants,no_products,products,reaction,no_spec)
        call check_atom_balance(reaction,no_spec)
end subroutine
```

```
subroutine set_reaction(no_reactants,reactants,no_products,products,reaction,no_spec)
     ! Example for one species reactant (nr) and one species product (np)

        nr = 1; np = 1; no_spec = nr + np
        do ireact = 1,no_reactants
        do iprod = 1,no_products
            call matrix_of_atom(reactants(ireact),products(iprod),neq,no_spec,coeff_mat,
                rhs_mat)
            call lineq_solver(neq,coeff_mat,rhs_mat,x_mat,flag)
                if (flag /= 0) cycle
        end do
        end do
            reaction%species(1:nr) = reactants(1:nr)
            reaction%species(nr+1:np) = products(1:np)
            reaction%coeff(1:no_spec) = x_mat(1:no_spec)
end subroutine
```

Program *Evaluate*

Evaluator comprises enthalpy and free energy change calculation to investigate the feasibility of the reactions. This program also contains other property values to be used for general information such as boiling point, heat capacity, critical properties and molecular weight. The program reads each reaction from *filename.reaction* and parses it using a parser program into individual species with respective coefficients. The results are stored in *filename.dat*. The structure of the program is given below.

```
program Evaluate_Reaction_Feasibility
      do
          read reaction
          call reaction_parser(reaction,no_spec,spec_name,spec_coeff)
          call thermo_calculation(no_spec,spec_name,spec_coeff,hreact,gibreact)
              param = 0 kJ/mol; 10 kJ/mol; 40 kJ/mol
              if (gibreact > param) cycle
      if (status /= 0) exit
      end do
end program
```

Chapter 4

Comparison with Experimental Work

4.1 Introduction

To test the validity of the approach, a number of case studies were performed on selected known chemical processes. The studies were conducted in three stages, due to different objectives of the problem. The first part consisted of preliminary investigation of a number of possible reactions and their thermodynamic requirements. The reactions were chosen from known process chemistry. The task was particularly aimed at testing relationship between possible reactions and negative free energy changes of reaction. Studies were performed on methane chlorination, hydrodealkylation of toluene and hydrogen cyanide manufacture.

The second part comprised two comparative studies of experimental work on partial wet oxidation of p-coumaric acid (Mantzavinos[42] & Herrera[43]) and alkylation of toluene with ethanol (Walendziewski[44]). The task was aimed at automated construction of reaction networks and its comparison with those obtained from the experiments. The criteria of feasibility defined in the first part were employed at this stage. The first two parts are described in this Chapter.

The third stage was the application of the program in chemical processes to investigate side reaction generation and its trailing effects. Beside species generation, the task also emphasized separation simulation, where the separability of components based on their boiling points were determined. Studies and discussions of this subject are described in Chapter 5.

4.2 Studies on free energy changes of several reactions

These preliminary studies involved simple reactions for which published information was available. Thermodynamic requirements of the chemical reactions were studied to establish the relation of negative free energy changes and existing reactions. According

to the principles of chemical equilibrium, spontaneous reactions occur when the value of free energy change is negative. Positive free energy changes correspond to a very small equilibrium conversion so as the formation of products is not apparent. However, a slightly positive free energy has been used empirically and from the commercial standpoint, feasible reactions may take place at slightly positive value, i.e. 40 kJ/mol (or 10 kcal/mol) as used in May & Rudd[6]. We use slightly positive free energy changes as a tuning criterion to investigate the sensitivity of species formation. In these initial studies, a condition of plausibility was established where free energy changes (ΔG) were calculated within two conditions :

- Temperatures were restricted at 298 K, but constraints on free energies were relaxed. Feasible reactions were measured at maximum ΔG = 40 kJ/mol.

- Free energies were maintained at negative values, while temperatures were elevated within the range of 298 K up to 1500 K.

These were illustrated on three common industrial reactions.

1. Chlorination of methane to produce monocholoromethane, methylene dichloride, chloroform or carbon tetrachloride

2. Hydrodealkylation of toluene to produce benzene

3. Production of hydrogen cyanide from methane and ammonia

In the following discussion, the reactions are divided into two main categories :

- *Category 1.* Reactions that should definitely take place having negative free energy change (ΔG < 0)

- *Category 2.* Reactions that are not likely to occur, having positive free energy change (ΔG > 0)

However, two other conditions were observed specified as categories 3 and 4, viz.

- *Category 3.* Reactions that are known to occur, but have positive free energy change

- *Category 4.* Reactions that are known not to occur but have negative free energy change

The following are the reaction summary and the free energy changes, both in standard condition (298 K) and elevated temperature. To simplify notation, standard conditions are not subscripted in this work.

4.2.1   Chloromethanes

Chlorination reactions of methane occur in the presence of light or heat above 400 °C. Usually, a catalyst is used to control the yield of either monocholoromethane, methylene dichloride, chloroform or carbon tetrachloride. The yield based on methane ranges from 85 - 90 %, and that of chlorine ranges from 99 - 100 %. Successive chlorination reactions of methane are shown below.

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$
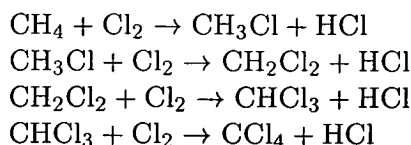
Free energy calculations on some obviously possible reactions give the following results.

1. *Category 1.* Reactions that should take place, $\Delta G < 0$

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	$\Delta G = -98.85$ (kJ/mol)
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$	$\Delta G = -107.26$ (kJ/mol)
$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$	$\Delta G = -109.70$ (kJ/mol)
$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$	$\Delta G = -101.98$ (kJ/mol)
$CH_3Cl \rightarrow HCl + CH_3CH_2Cl$	$\Delta G = -32.52$ (kJ/mol)
$CH_3CH_2Cl + Cl_2 \rightarrow HCl + CH_3CHCl_2$	$\Delta G = -109.70$ (kJ/mol)
$2\ CH_2Cl_2 \rightarrow HCl + ClCH_2CHCl_2$	$\Delta G = -34.96$ (kJ/mol)
$CH_3CH_2Cl + Cl_2 \rightarrow HCl + ClCH_2CH_2Cl$	$\Delta G = -107.26$ (kJ/mol)
$ClCH_2CH_2Cl \rightarrow HCl + CH_2{=}CHCl$	$\Delta G = 4.4$ (kJ/mol)
At elevated temperature :	$\Delta G_{400K} = -10.82$ (kJ/mol)

2. *Category 2.* Reactions that should not occur have $\Delta G > 0$

$2\ CH_4 \rightarrow CH_3CH_3 + H_2$	$\Delta G = 67.70$ (kJ/mol)
$CH_3Cl + HCl \rightarrow CH_2Cl_2 + H_2$	$\Delta G = 83.40$ (kJ/mol)
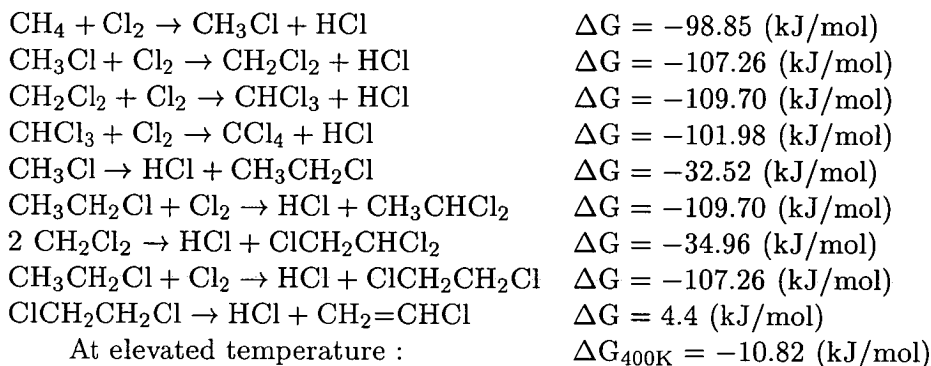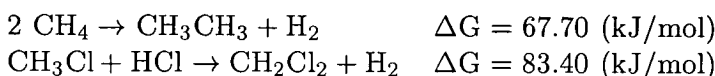
3. *Category 4.* Reactions that are not known but have $\Delta G < 0$

$CH_4 + Cl_2 \rightarrow CH_2Cl_2 + H_2$	$\Delta G = -15.45$ (kJ/mol)
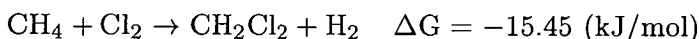
The study of chloromethane reactions shows that reactions participate in the chlorination process apparently have negative free energy changes. Conversely, reactions that are not known to occur although stoichiometrically plausible have positive free energy changes. From the list in Category 1, it can be seen that beside the main reactions, other side reactions leading to the formation of chloroethane, dichloroethane, ethylenedichloride and vinylchloride were found. These results are in agreement with the principal byproducts found in industry[57].

However, an exception is found in Category 4 which contains an unexpected reaction with negative free energy changes. The explanation for this situation can be made from the chemistry of the reaction. It is unlikely that methane releases two hydrogen atoms at once and substitutes them with two chlorine atoms. The reaction might be the summation of several reactions such as :

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$	$\Delta G = -98.85$ (kJ/mol)
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$	$\Delta G = -107.26$ (kJ/mol)
$2\ HCl \rightarrow H_2 + Cl_2$	$\Delta G = 190.66$ (kJ/mol)
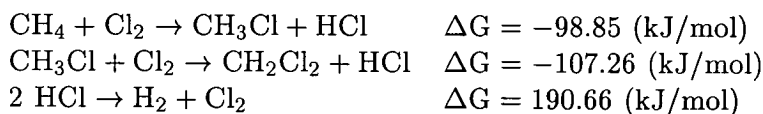
The net reaction is equal to that of the reaction in Category 4, and the total free energy changes of those reactions is -15.45 kJ/kmol. But it can also be seen that reaction 3 has a positive free energy change. Therefore, in order for a reaction to be considered plausible, the chemistry of the reaction must be taken into account. This indicates a weakness in our approach, and confirms that any result on new processes should be considered very carefully.

4.2.2 HDA Process

The hydrodealkylation of toluene into benzene takes place under catalytic or high thermal conditions. The operating temperatures range from 500 - 595 °C and the operating pressures are usually from 4 to 6 bar. Benzene is the desired product. In HDA process, there are two main reactions[5, 56] :

$$C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$$
$$2C_6H_6 \rightleftharpoons C_6H_5.C_6H_5 + H_2$$
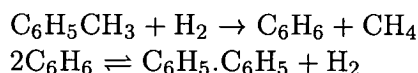
Calculation of the free energy changes on some related reactions show the following results.
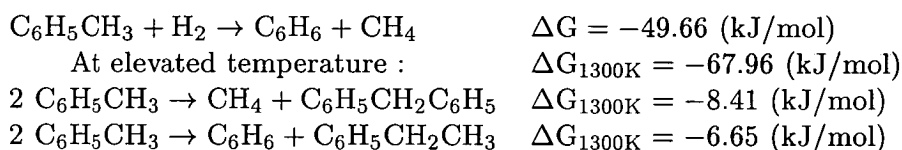
1. *Category 1.* Reactions that should take place, $\Delta G < 0$

   $C_6H_5CH_3 + H_2 \rightarrow C_6H_6 + CH_4$ $\Delta G = -49.66$ (kJ/mol)
        At elevated temperature : $\Delta G_{1300K} = -67.96$ (kJ/mol)
   $2\ C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2C_6H_5$ $\Delta G_{1300K} = -8.41$ (kJ/mol)
   $2\ C_6H_5CH_3 \rightarrow C_6H_6 + C_6H_5CH_2CH_3$ $\Delta G_{1300K} = -6.65$ (kJ/mol)

2. *Category 2.* Reactions that should not occur having $\Delta G > 0$

   $C_6H_5CH_3 + CH_4 \rightarrow C_6H_4CH_3CH_3 + H_2$ $\Delta G = 49.66$ (kJ/mol)
        At elevated temperature : $\Delta G_{1300K} = 64.61$ (kJ/mol)
   $C_6H_5CH_3 + CH_4 \rightarrow C_6H_4CH_2CH_3 + H_2$ $\Delta G = 59.29$ (kJ/mol)
        At elevated temperature : $\Delta G_{1300K} = 69.14$ (kJ/mol)
   $C_6H_6 + CH_4 \rightarrow C_6H_5CH_3 + H_2$ $\Delta G = 49.66$ (kJ/mol)

3. *Category 3.* Reactions that are known to occur, but $\Delta G > 0$

   $C_6H_6 \rightleftharpoons C_6H_5C_6H_5 + H_2$ $\Delta G = 31.62$ (kJ/mol)
        At elevated temperature : $\Delta G_{1300K} = 61.10$(kJ/mol)
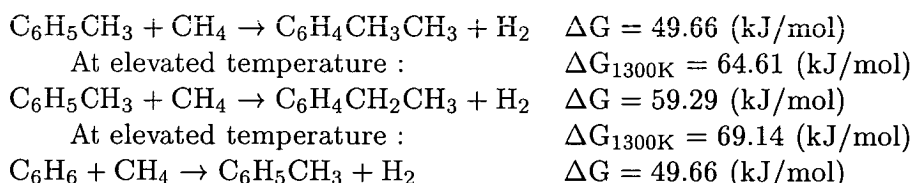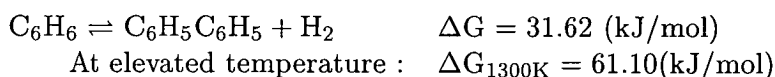
Reactions in categories 1 and 2 have straightforward explanations. Reaction in category 3 involves the conversion of benzene to diphenyl in the form of reversible reaction. The reaction occurs despite positive ΔG, and it is well known that benzene undergoes dehydrocondensation at high temperature producing small amount of biphenyls and terphenyls. Reaction in category 3 is known to occur despite the positive ΔG. This concurs with the condition of plausibility set out previously where the maximum free energy change criteria is 40 kJ/mol (10 kcal/mol)[6]. Thus, reactions having small positive ΔG are acceptable and regarded as feasible.

Beside the main reactions, several side reactions were generated by our program. However the production of byproducts are not reported elsewhere, possibly because the selectivity of the desired products is much higher compared to other side reactions.

4.2.3 Hydrogen Cyanide Reaction

Hydrogen cyanide is manufactured by the following methods[46, 55] :

1. The Andrussow process requires the reaction of methane, ammonia and oxygen carried out over a platinum or platinum-rhodium catalyst at elevated temperature, i.e about 1100 °C.

$$CH_4 + NH_3 + 1.5 \ O_2 \rightarrow HCN + 3 \ H_2O$$
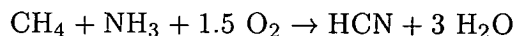
2. The Degussa process is performed in the absence of air at 1400 °C in a series of small ceramic tubes whose inner surfaces are coated with platinum.

$$CH_4 + NH_3 \rightarrow HCN + 3 \ H_2$$
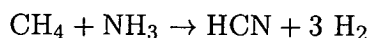
Both processes yield above 85 - 90 % hydrogen cyanide.

4.2.4 The Andrussow Process

In Andrussow process, there are three categories of chemical reactions.

1. *Category 1.* Reactions that should take place, $\Delta G < 0$

$CH_4 + NH_3 + 1.5 \ O_2 \rightarrow HCN + 3 \ H_2O$	$\Delta G = -499.17$ (kJ/mol)
$CH_4 + 2 \ O_2 \rightarrow CO_2 + 2 \ H_2O$	$\Delta G = -801.33$ (kJ/mol)
$CH_4 + 1.5 \ O_2 \rightarrow CO + 2 \ H_2O$	$\Delta G = -544.13$ (kJ/mol)
$2 \ NH_3 + 1.5 \ O_2 \rightarrow N_2 + 3 \ H_2O$	$\Delta G = -654.08$ (kJ/mol)
$H_2 + 0.5 \ O_2 \rightarrow H_2O$	$\Delta G = -228.80$ (kJ/mol)
$2 \ NO + O_2 \rightarrow 2 \ NO_2$	$\Delta G = -149.98$ (kJ/mol)
$NH_3 + O_2 \rightarrow NO + H_2O + 0.5 \ H_2$	$\Delta G = -100.60$ (kJ/mol)
$2 \ NH_3 \rightarrow 3 \ H_2 + N_2$	$\Delta G = 32.32$ (kJ/mol)
At elevated temperature :	$\Delta G_{500K} = -10.10$ (kJ/mol)
$CH_4 + O_2 \rightarrow CO_2 + 2 \ H_2$	$\Delta G = -343.73$ (kJ/mol)
$HCN + NH_3 \rightarrow N_2 + CH_4$	$\Delta G = -154.91$ (kJ/mol)
$CH_4 + NH_3 \rightarrow HCN + 3 \ H_2$	$\Delta G = 187.23$ (kJ/mol)
At elevated temperature :	$\Delta G_{1100K} = -10.34$ (kJ/mol)
$CH_4 + O_2 \rightarrow CO_2 + 2 \ H_2$	$\Delta G = -343.73$ (kJ/mol)
$HCN + H_2O \rightarrow CO + NH_3$	$\Delta G = -44.96$ (kJ/mol)
$CO + H_2O \rightarrow CO_2 + H_2$	$\Delta G = -28.40$ (kJ/mol)
$2 \ NO \rightarrow O_2 + N_2$	$\Delta G = -228.04$ (kJ/mol)
$2 \ NO + 2 \ H_2 \rightarrow 2 \ H_2O + N_2$	$\Delta G = -681.68$ (kJ/mol)
$4 \ NH_3 + 5 \ O_2 \rightarrow 4 \ NO + 6 \ H_2O$	$\Delta G = -860.00$ (kJ/mol)
$4 \ NH_3 + 6 \ NO \rightarrow 5 \ N_2 + 6 \ H_2O$	$\Delta G = -1980.40$ (kJ/mol)
$2 \ NO + 2 \ CO \rightarrow N_2 + 2 \ CO_2$	$\Delta G = -738.48$ (kJ/mol)

2. *Category 2.* Reactions that should not take place having $\Delta G > 0$

$NH_3 + O_2 \rightarrow NO_2 + 1.5 \ H_2$	$\Delta G = 53.21$ (kJ/mol)
$N_2 + 2 \ O_2 \rightarrow 2 \ NO_2$	$\Delta G = 74.10$ (kJ/mol)
$N_2 + O_2 \rightarrow 2 \ NO$	$\Delta G = 224.08$ (kJ/mol)
$CH_4 + NH_3 \rightarrow CH_3NH_2 + H_2$	$\Delta G = 91.02$ (kJ/mol)
$CH_4 + HCN \rightarrow CH_3CN + H_2$	$\Delta G = 29.81$ (kJ/mol)
$CH_4 + H_2O \rightarrow CO + 3 \ H_2$	$\Delta G = 142.27$ (kJ/mol)
$2 \ CH_4 \rightarrow CH_3CH_3 + H_2$	$\Delta G = 67.70$ (kJ/mol)

The presence of oxygen in the Andrussow process is necessary to achieve the complete conversion of hydrogen. The main reaction is endothermic, but by oxidizing part of methane, the overall process becomes exothermic. The reaction is carried out adiabatically, and decomposition of hydrogen cyanide is avoided by quenching the off-gas immediately to below 400 °C.

The feed components are known to decompose into coke, nitrogen, hydrogen and oxygen forming hydrogen cyanide and other species which come as byproducts. The yield of hydrogen cyanide from ammonia is about 80 %. Based on this data, it is estimated that the composition of the converter off-gas is as follows : nitrogen 49.9 %, water 21.7 %, hydrogen 13.5 %, hydrogen cyanide 8.1 %, carbon monoxide 3.7 %, carbon dioxide 0.2 %, methane 0.6 % and ammonia 2.3 %.

Reactions found in this process are complicated as seen in Category 1. At higher temperatures, more oxidation occurs toward nitrogen and carbon. Components resulting from these oxidation reactions comprise some intermediate such as NO and CO which were further oxidized or react with other species to form more stable components. These are consisting of NO_2, CO_2, N_2 and H_2. In experimental and modeling studies of HCN synthesis from methane, ammonia and oxygen performed by Hasenberg et al[48], 15 reactions were identified. Other workers such as Waletzko et al[47] has found the first 13 reactions and McKenna et al[46] 14 reactions. The reactions found in their work are as follows :

$$NH_3 \rightarrow 1.5\ H_2 + 0.5\ N_2$$
$$NH_3 + CH_4 \rightarrow HCN + 3\ H_2$$
$$NH_3 + 1.25\ O_2 \rightarrow NO + 1.5\ H_2O$$
$$NH_3 + 1.5\ NO \rightarrow 1.25\ N_2 + 1.5\ H_2O$$
$$0.5\ O_2 + H_2 \rightarrow H_2O$$
$$CH_4 + 1.5\ O_2 \rightarrow CO + 2\ H_2O$$
$$NO + H_2 \rightarrow 0.5\ N_2 + H_2O$$
$$NO \rightarrow 0.5\ N_2 + 0.5\ O_2$$
$$NO + CO \rightarrow 0.5\ N_2 + CO_2$$
$$CO + 0.5\ O_2 \rightarrow CO_2$$
$$CH_4 + NO \rightarrow HCN + 0.5\ H_2 + H_2O$$
$$CO + H_2O \rightarrow CO_2 + H_2$$
$$CH_4 + 3\ NO \rightarrow 1.5\ N_2 + CO + H_2O$$
$$HCN + H_2O \rightarrow NH_3 + CO$$
$$CH_4 + 4\ NO \rightarrow 2\ N_2 + CO_2 + 2\ H_2O$$
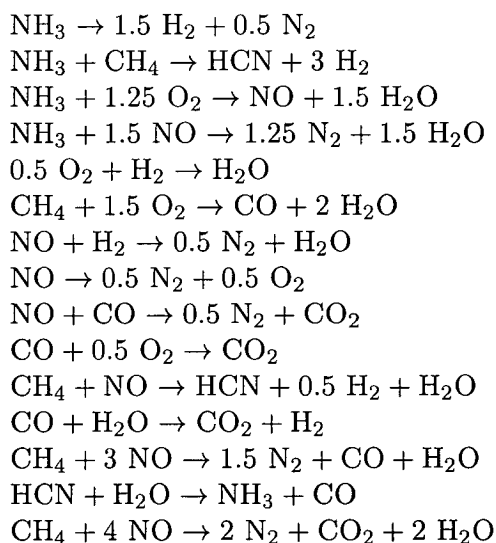
The reactions listed above are the dominant steps in producing HCN which can also be generated from our program. Other reactions not found in the list but generated in this program, such as reaction 1 and 2 listed in *Category 1*. The reactions are probably the summation of several reactions. Since the reaction temperature is relatively high, species decompositions are possible. However, further decomposition reactions were not looked at in the experimental work conducted by other researchers. As for coke formation, our program does not allow pure carbon generation. It is assumed that carbon reacts with oxygen to form carbon monoxide and carbon dioxide. Therefore, the decomposition products exclude carbon. This is also observed in the experimental

work where coke formation is not reported.

4.2.5 The Degussa process

Reactions in Degussa process consists of the following categories :

1. *Category 1.* Reactions that are known to occur, at standard condition $\Delta G > 0$ but negative at high temperature.

   $CH_4 + NH_3 \rightarrow HCN + 3\, H_2$ $\quad \Delta G = 187.23$ (kJ/mol)

   $\quad$ At elevated temperature : $\quad \Delta G_{1100K}^{} = -10.34$ (kJ/mol)

   $2\, NH_3 \rightarrow 3\, H_2 + N_2$ $\quad \Delta G = 32.32$ (kJ/mol)

   $\quad$ At elevated temperature : $\quad \Delta G_{500K} = -10.10$ (kJ/mol)

2. *Category 2.* Reactions that should not take place having $\Delta G > 0$

   $CH_4 + NH_3 \rightarrow CH_3NH_2 + H_2$ $\quad \Delta G = 91.02$ (kJ/mol)

   $CH_4 + HCN \rightarrow CH_3CN + H_2$ $\quad \Delta G = 29.81$ (kJ/mol)

   $2\, CH_4 \rightarrow CH_3CH_3 + H_2$ $\quad \Delta G = 67.70$ (kJ/mol)
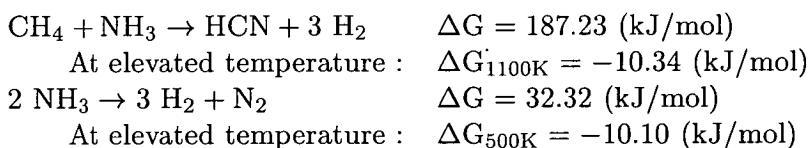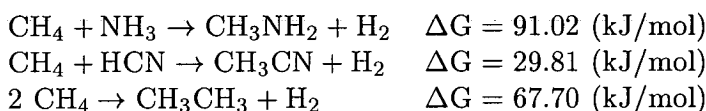
In the Degussa process, air is omitted letting ammonia and methane react directly. The number of reactions derived from the main reaction and the amount of components in the off-gas are much less compared to the process with oxygen. Degussa process produces 90 % yield of hydrogen cyanide from ammonia. The off-gas of the converter contains 20 % HCN, 70 % hydrogen, 3 % ammonia, 1 % methane and 1 % nitrogen as a result of ammonia decomposition.

Other investigators[46, 49, 50] experimenting HCN synthesis from methane and ammonia identified the important reactions that take place, these are decomposition reactions of methane and ammonia and synthesis of HCN as shown below. Other side reactions were not observed.

$$CH_4 + NH_3 \rightarrow HCN + 3\, H_2$$
$$2\, NH_3 \rightarrow 3\, H_2 + N_2$$
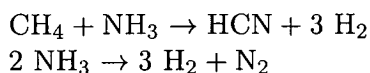
The experimental results are similar to those generated by our program. Other byproducts are not generated.

4.2.6 Summary

A number of possible reactions have been derived from three particular processes and the values of free energy changes have been calculated. The results are in agreement with the existing conditions found in the industries, namely reactions which are known to occur have negative free energy changes and those which are not known to occur have positive free energy changes. This shows that for practical purposes, equilibrium condition or free energy changes can be considered as a means to quickly determine the occurence of a reaction. However, there is certain reaction which is known to occur but having positive free energy change, such as the conversion of benzene to diphenyl in the HDA process which is 31 kJ/mol. As it is mentioned earlier, slightly positive free energy has been used empirically for commercial purpose. Therefore, the condition of

plausibility defined at the beginning of this section, seems to be reasonable to justify the feasibility of reactions. Hence, the maximum free energy changes for a feasible reaction is set at 40 kJ/mol. In the present work, free energy changes are considered as threshold values and will be used further as a tuning criterion, to determine the sensitivity of reaction generation. The sensitivity analysis is performed under various threshold values, see Section 4.3.3 for detail.

4.3 Comparison with experiments

4.3.1 Partial Wet Oxidation of p-Coumaric Acid

Experimental work on wet oxidation of p-coumaric acid conducted by Mantzavinos & Herrera were adopted for this program. p-coumaric acid ($OHC_6H_4CH=CHCOOH$) is a complex structure of the polyphenolic fraction found in the waste effluent of olive oil processing and wine distilleries. A side chain of acid has a double bond attached at the para position to phenyl.

p-coumaric acid
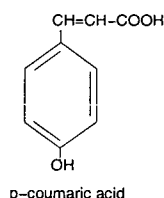
In wet oxidation reaction, both side chains and aromatic ring will be destroyed. The aromatic ring discloses and fractures into ring cleavage components with 1 to 4 carbon atoms. Since side chain bonds are weaker than ring bonds, attacks by oxidizing agents occur at the side chain first keeping the aromatic ring intact. The side chain undergoes fragmentation accompanied by electrophilic substitution. This is followed by destruction of aromatic ring. The mechanisms of wet oxidation reaction of this component were constructed based on postulations conceived below. The oxidizing species compose of hydroxyl radicals generated by hydrogen abstraction on H_2O molecule.

Based on its structure which exhibits the properties of double bonds and carboxyls, the mechanisms of wet oxidation of phenolic compounds may correspond to the behaviour of acid, alkene, aldehyde and alcohol under oxidation reaction. The side chain of p-coumaric acid is reduced by double bond fission and acid bond decarboxylation. The structure is immediately transformed into a simpler form such as p-hydroxybenzaldehyde, p-vinyl phenol, glyoxylic acid and carbon dioxide. The following figure illustrates the structure of these components.

p-hydroxybenzaldehyde   p-hydroxybenzoic   p-vinyl phenol   p-cresol   glyoxylic acid
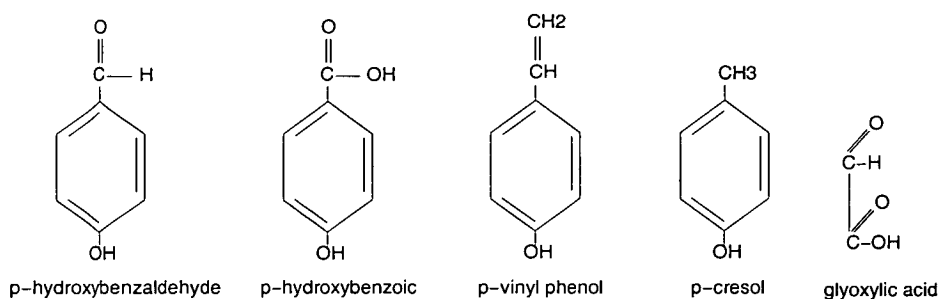
To enable the destruction of the aromatic ring by oxidation at normal experimental condition, all carboxyls must be knocked down first and the structure is reduced to that with non-oxidative side chains such as phenol or hydroquinone. Devlin's mechanisms (Devlin[45]) for aqueous phenol destruction has been adapted for building up rules on breaking up the aromatic ring. According to Devlin, the formation of hydroquinone from phenol initiates the ring opening which leads to the formation of 2,5-dioxo-3-hexenedioic acid and muconic acid. Subsequent decarboxylations reduce the chain length producing refractory intermediate materials such as gluoxal, glyoxic acid, oxalic acid and so on.

For the aromatic ring fragmentation, besides following the mechanisms proposed by Devlin, we used a 'sledghammer' technique where the ring is broken randomly. The followings are the radicals that might be obtained from an aromatic ring.

1. Open up benzene ring by replacing side chains with acids and hydrogen to produce $COOHCH=CHCH=CHCOOH$ and $CH_2=CHCH=CHCH=CH_2$.

2. Break down benzene ring into radicals having one to five atom C, such as $\dot{C}HCH$, $CH_3\dot{C}\dot{C}H$, $\dot{C}H=\dot{C}H$, $\dot{C}H_2$, $\dot{C}H_2=CHCH=\dot{C}H_2$ and $\dot{C}H_2CH=CHCH=\dot{C}H_2$. These radicals would react with oxygen, hydrogen or hydroxyl and produce components like CH_4, $OHCH=CHCH=CH_2$, $CHOCH=CH_2$, $CH_2=CHCH=CH_2$, CH_3COCHO, $CH_2=CH_2$, CH_3OH, $CHOCHO$.

The above mechanisms are embodied in the program in the form of rules or procedures. Since each compound belongs to a certain chemical class, the reactive behaviour of the class can be formulated and written in modular programming structures. In this case study, species and reactions are generated by creating inferences from the rules of wet oxidation reaction on complex phenolic structure. Hence, by enumerating all functional groups, the program is able to identify the exact structure of the compound and decide the types of reactions. Components undergo different activation according to the type of functional groups found in them.

In this study, reaction temperature was taken into account since it is associated with the condition of plausibility previously mentioned in section 4.2. The calculation of the reaction free energy changes were varied within the range of 298 to 500 K, in accordance with moderate thermal conditions under which the experimental studies were conducted. The reaction temperatures of the experiments were set at 403, 423,

453 and 523 K in a high pressure reactor, i.e. up to 100 bar.

The results of the present work show that all components found in the experimental works conducted by Mantzavinos & Herrera were generated. The formation of new components at each sequence is illustrated in Figure 4.1 in the form of species tree diagram. The species tree is divided into levels and nodes. A level indicates each generation of species which is also called the depth of expansion, and a node indicates a species (See section 3.3). In this program, **Level 1** always deals with the exploration of the starting species. Components enclosed in brackets in the initial reactants denote oxidizing agents. The following section describes species transformation involving all feasible reactions with the values of free energy changes.

LEVEL 1

The starting species which consisted of p-coumaric acid, water and oxygen produced the following radicals and 8 new species.

Radicals of component	{OH}C6H4CH:CH:COOH				5
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 CHCOOH		-2	T	2	2
2 {OH}C6H4CH		-2	F	1	1
3 {OH}C6H3CH:CH:COOH		-1	F	4	4
4 {OH}C6H4CH:CH:		-1	F	1	0
5 C		-4	T	1	0

Radicals of component	O2				1
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 O		-2	T	1	1

Radicals of component	H2O				2
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 H		-1	T	1	0
2 HO		-1	T	2	0

New products	8
1	OHCH2COOH
2	H2
3	{OH}C6H4CH2OH
4	{OH}C6H4CH:CH2:
5	CHOCOOH
6	{OH}C6H4CHO
7	CO2
8	{OH}C6H4CH:CH:OH
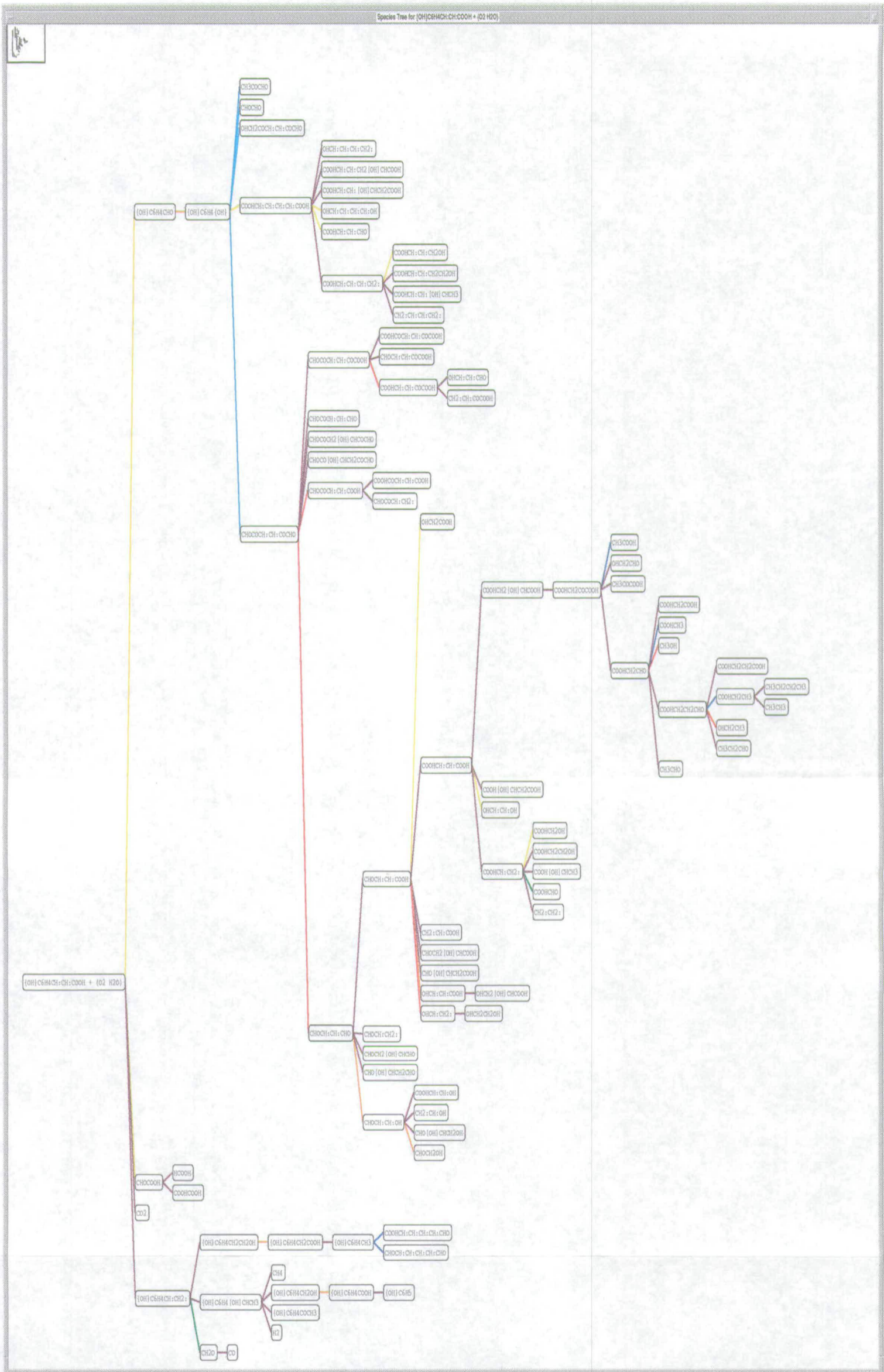
Figure 4.1: Graphical view of the expansion of nodes on the wet oxidation of p-coumaric acid
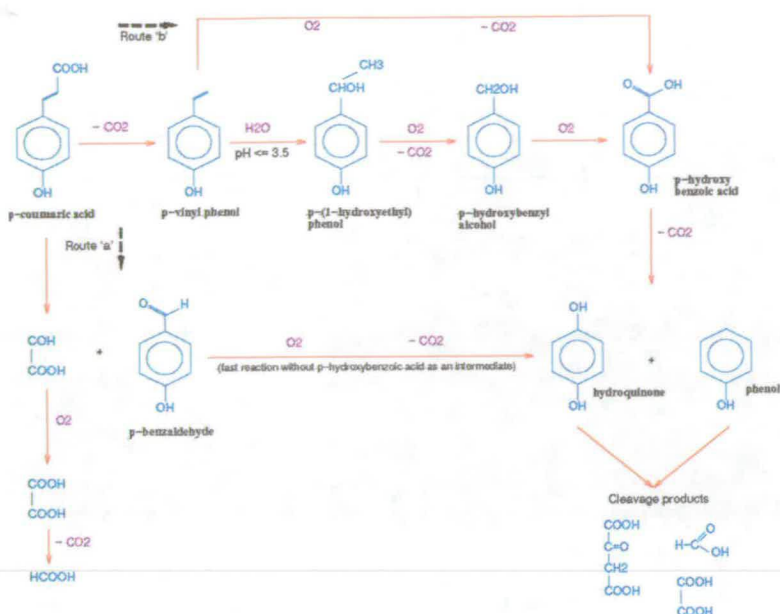
Figure 4.2: Reaction network for the oxidation reaction of p-coumaric acid[42]

and lastly phenol. Phenol will undergo openchain reaction and be reduced into oxaloacetic acid, oxalic acid, formic acid etc.

In **Level 1**, the species and reactions were generated based on functional groups found in coumaric acid. Four functional groups were identified, i.e. carboxyl, double bond, phenol and aromatic given in the order of stability. When oxidation reaction was applied to those structures, procedures relevant to the behaviour of those groups under oxidation reaction were invoked. Such procedures are described in the following manner.

- Decarboxylation
  This procedure was carried out when a carboxyl group was recognized. The carboxyl group ('COOH' or 'CHO') was detached and lost into CO_2. The rest of the component was hydrolyzed and it would be reduced by one carbon atom.

- Double bond cleavage
  When a double bond was identified, several oxidative cleavages occur depend on the location of the double bond, such as :

  - Carbon-carbon cleavage leads to the formation of aldehyde, this occurs when double bond is possessed by primary or secondary carbons
  - Carbon-carbon cleavage leads to the formation of ketone, this occurs when double bond is possessed by tertiary carbons
  - Double bond reduction to single bond leads to the formation of alcohol
  - Double bond rupture leads to the formation of aldehyde and alcohol

Having generated a number of new species based on the above rules, stoichiometrically plausible reactions were established, followed by the evaluation of the free energy

changes. Reactions which did not have negative free energy changes were then eliminated. Therefore, components which were generated based on the above rules may not appear in the surviving species.

The procedures were then applied to each surviving species producing the next generation of components. At **Level 2**, the following nodes were explored. The formation of radicals is shown for node 1 only, while the rest is available in Appendix E .

LEVEL 2

1. Node 1 : the reaction of OHC_6H_4CHO

Radicals of component   {OH}C6H4CHO   14

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	CH2:CH:CH:CH:CHCH2	-2	F	1	2
2	H	-1	T	1	0
3	CH2	-2	T	1	1
4	CH2:CH:CH:CH:CH	-2	F	1	1
5	CH:CH:CH:CH:	-2	T	1	4
6	CH:CH:	-2	T	1	2
7	CHCH	-4	F	1	2
8	CH2:CH:CHCHCH:CH2:	-2	F	3	4
9	CHCH:CH2:	-2	T	3	3
10	CH3CCH	-4	F	1	2
11	CH2CH:CH:CH:CH:CH2	-2	F	1	6
12	COCH:CH:CH:CH:CO	-2	F	1	6
13	CHCOCH:CH:COCH	-4	F	1	6
14	{OH}C6H4CO	-1	F	1	0
15	{OH}C6H4	-1	F	1	0
16	C	-4	T	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

New products   26
        1   CH2:CH:CH:CH:CH:CH2:

2	H2
3	CH3OH
4	OHCH:CH:CH:CH2:
5	OHCH:CH:CH:CH:OH
6	OHCH:CH2:
7	OHCH:CH:OH
8	OHCH2CH2OH
9	OHCH2CH:CH2:
10	CH3[OH]CHCH2OH
11	OHCH2CH:CH:CH:CH:CH3
12	OHCH2CH:CH:CH:CH:CH2OH
13	COOHCH:CH:CH:CH:CHO
14	COOHCH:CH:CH:CH:COOH
15	{OH}C6H5
16	CH2O
17	CHOCHO
18	CHOCH:CH2:
19	CH3COCHO
20	CHOCOCH:CH:COCHO
21	CO2
22	{OH}C6H4COOH
23	{OH}C6H4{OH}
24	OHCH2CHO
25	CH3[OH]CHCHO
26	OHCH2COCH:CH:COCHO

Three feasible reactions transforming aldehyde group to carboxylate and hydroxyl groups were generated from the above species.

(a) $OHC_6H_4CHO + H_2O \rightarrow H_2 + OHC_6H_4OH$
$\Delta G_{298K} = -448.49(kJ/mol)$

(b) $OHC_6H_4CHO + H_2O \rightarrow OHC_6H_5 + CO_2$
$\Delta G_{298K} = -65.07(kJ/mol)$

(c) $OHC_6H_4CHO + H_2O \rightarrow H_2 + OHC_6H_4COOH$
$\Delta G_{298K} = -15.59(kJ/mol)$
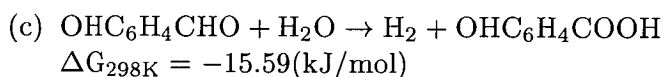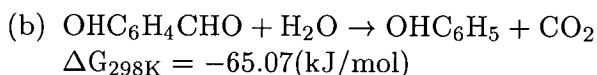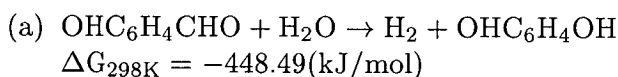
The surviving species obtained from this level were OHC_6H_4OH, OHC_6H_5, CO_2, H_2 and OHC_6H_4COOH. The conversion of p-hydroxybenzaldehyde into phenol and hydroquinone had high negative free energy change, which indicated that aldehyde group may be detached from the main group. Reaction (c) was not detected during the experiment. The results also show that the value of free energy change of the decarboxylation of aldehyde group is much lower than that of the conversion of aldehyde into carboxylate, thus indicates that the selectivity toward reaction (a) in particular is high. Perhaps this is the reason for the inhibition of reaction 3. In the experiment, p-hydroxy benzoic acid was formed through another route.

2. Node 2 : the reaction of CHOCOOH

   (a) $CHOCOOH + O_2 \rightarrow H_2O + 2\ CO_2$
   $\Delta G_{298K} = -540.53(kJ/mol)$

   (b) $CHOCOOH + H_2O \rightarrow H_2 + COOHCOOH$
   $\Delta G_{298K} = -15.59(kJ/mol)$

   (c) $CHOCOOH + H_2O \rightarrow 2\ H_2 + 2\ CO_2$
   $\Delta G_{298K} = -82.93(kJ/mol)$

   (d) $CHOCOOH + H_2O \rightarrow H_2 + CO_2 + HCOOH$
   $\Delta G_{298K} = -39.53(kJ/mol)$

   (e) $CHOCOOH + H_2O \rightarrow 2\ HCOOH$
   $\Delta G_{298K} = 3.87(kJ/mol)$

   Surviving species emerged from this level were H_2, H_2O, CO_2, HCOOH and COOHCOOH. They were generated by the oxidation of the aldehyde group and decarboxylation. The experiments showed different conversion of CHOCOOH, that is by a reaction with O2. This requires two moles CHOCOOH to react with one mole O2, while the program does not allow the total reactant coefficients to be greater than two. However, similar final products such as HCOOH, CO_2 and H_2 were found in the experiments.

3. Node 3 : oxidation reaction of CO_2 which produces no new species since carbon dioxide is considered as an ultimate species.

4. Node 4 : oxidation of p-vinyl phenol

   (a) $OHC_6H_4CH{=}CH_2 + O_2 \rightarrow CH_2O + OHC_6H_4CHO$
   $\Delta G_{298K} = -305.78(kJ/mol)$

   (b) $OHC_6H_4CH{=}CH_2 + H_2O \rightarrow OHC_6H_4[OH]CHCH_3$
   $\Delta G_{298K} = 1.70(kJ/mol)$

   (c) $OHC_6H_4CH{=}CH_2 + H_2O \rightarrow OHC_6H_4CH_2CH_2OH$
   $\Delta G_{298K} = 4.14(kJ/mol)$

   The oxidation of p-vinyl phenol resulted in the formation of p-hydroxy benzaldehyde, p-2,hydroxy benzyl alcohol and p-1,hydroxy benzyl alcohol. Similar results were found in the experimental work, except for p-1,hydroxy benzyl alcohol which was not generated. The tendency of the reaction was towards structure p-2.

Having explored all nodes in **Level 2**, expansion in **Level 3** proceeds by generating new species from the surviving species of **Level 2**. The reactions found in **Level 3** are presented below.

LEVEL 3

1. Node 1 : expansion of CH_2O

   (a) $2\ CH_2O \rightarrow CO_2 + CH_4$
   $\Delta G_{298K} = -225.47(kJ/mol)$

    (b) $CH_2O \rightarrow CO + H_2$
        $\Delta G_{298K} = -27.40 (kJ/mol)$

    (c) $CH_2O \rightarrow CO_2 + H_2O$
        $\Delta G_{298K} = -513.40 (kJ/mol)$

    (d) $CH_2O + H_2O \rightarrow CO_2 + 2\ H_2$
        $\Delta G_{298K} = -55.80 (kJ/mol)$

The surviving species generated from this level were CO_2, CH_4, CO, H_2O and H_2. The formation of formaldehyde was not detected in the experimental network. This may be due to the rapid conversion of formaldehyde after its formation. p-coumaric acid was inclined to split to produce more stable p-hydroxy benzaldehyde and glyoxylic acid, and therefore observable.

Species in this node contained 1 atom carbon and is categorized as an ultimate species undergoing decomposition during oxidation reaction.

2. Node 2 : $OHC_6H_4[OH]CHCH_3$

    (a) $OHC_6H_4[OH]CHCH_3 \rightarrow H_2 + OHC_6H_4COCH_3$
        $\Delta G_{298K} = -1.75 (kJ/mol)$

    (b) $2\ OHC_6H_4[OH]CHCH_3 \rightarrow OHC_6H_4CH_2OH + CH_4 + OHC_6H_4COCH_3$
        $\Delta G_{298K} = -46.51 (kJ/mol)$

    (c) $OHC_6H_4[OH]CHCH_3 + O_2 \rightarrow H_2 + OHC_6H_4CH_2OH + CO_2$
        $\Delta G_{298K} = -400.58 (kJ/mol)$

The surviving species emerged from the exploration of this node consisted of 5 species as follows : $H_2, OHC_6H_4COCH_3, OHC_6H_4CH_2OH, CH_4, CO_2$.

Rules for building up reactions from such component were based on oxidation reaction of secondary alcohol and aromatic decomposition. The rules incorporated in the procedures consisted of the followings :

- Removal of the secondary alcohol group and its transformation to ketone

- Removal of an alkyl attached to carbon atom possessing 'OH'

- Split between carbon atom possessing 'OH'

- Aromatic decomposition

Dominant product generated in the experiment from this level is hydroxybenzylalcohol ($OHC_6H_4CH_2OH$) as indicated by large negative free energy change. Other reactions might not occur or the component was found in trace amount and therefore undetectable.

3. Node 3 : oxidation of oxalic acid (COOHCOOH)

    (a) $COOHCOOH \rightarrow CO_2 + HCOOH$
        $\Delta G_{298K} = -23.94 (kJ/mol)$

(b) $COOHCOOH \rightarrow H_2 + 2CO_2$
$\Delta G_{298K} = -67.34 (kJ/mol)$
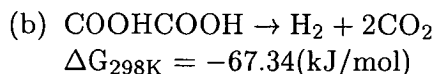
Surviving species generated from the above reactions were : CO_2 and $HCOOH$. Decarboxylation and decomposition procedures were applied to this component. The results were similar to that found in the experiments.

4. Node 4 : oxidation of OHC_6H_4OH

(a) $OHC_6H_4OH + O2 \rightarrow H_2 + CHOCOCH=CHCOCHO$
$\Delta G_{298K} = -189.46 (kJ/mol)$

(b) $OHC_6H_4OH + O2 \rightarrow COOHCH=CHCH=CHCOOH$
$\Delta G_{298K} = -340.18 (kJ/mol)$

(c) $OHC_6H_4OH + O2 \rightarrow H_2 + OHCH_2COCH=CHCOCHO$
$\Delta G_{298K} = -226.76 (kJ/mol)$

(d) $OHC_6H_4OH + O2 \rightarrow CH_2O + CHOCHO + CH_3COCHO$
$\Delta G_{298K} = -180.78 (kJ/mol)$
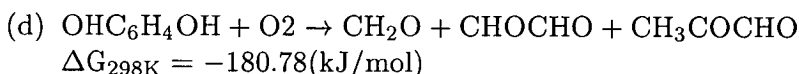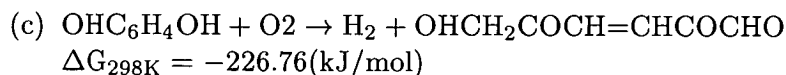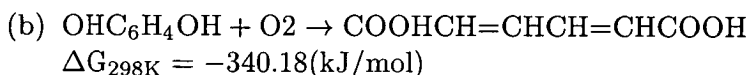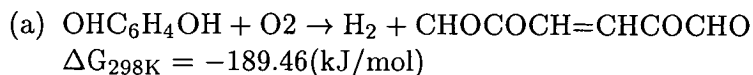
Hydroquinone undergoes similar oxidation reaction to phenol, ring opening occurred at this stage forming species with straight chain, diacid and double bonds.

The mechanisms of aromatic ring opening were established by following Devlin's mechanisms. In addition to that, the mechanisms were also constructed by random cleavage and random formation of functional groups especially of carbonyls which were considered reactive during oxidation. Apparently, the ring opening started with the production of straight chain compounds having 6 carbon atoms, although there was an exemption on reaction (d) Node 4. Reactions (a)-(c) generated compounds with carbonyl groups at both ends. As a whole, the results were in consistent with Devlin's study on phenol destruction. The reaction network of Devlin's experimental study can be seen in Figure 4.3. In his work, carbonyl groups were detached from the compounds and gradually reduced the number of carbon atoms down to four, three, two, one and finally carbon dioxide and water. Short chains were obtained mainly by the cleavage of the double bond.

5. Node 5 : oxidation of $OHC_6H_4CH_2CH_2OH$.

(a) $OHC_6H_4CH_2CH_2OH + O_2 \rightarrow OHC_6H_4CH_2COOH$
$\Delta G_{298K} = -435.89 (kJ/mol)$
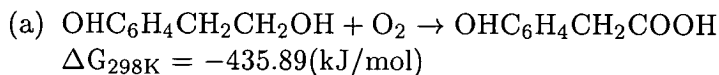
This route was not found in the experiments, which might be due to the reaction less competitive and only a trace amount of product generated.

6. Node 6 : HCOOH oxidation

Formic acid (HCOOH) underwent decomposition reaction producing carbon dioxide and hydrogen.

(a) $HCOOH \rightarrow CO_2 + H_2$
$\Delta G_{298K} = -43.40(kJ/mol)$
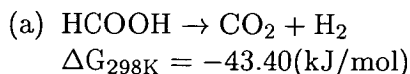
LEVEL 4

Level 4 expands further the surviving species generated in **Level 3**. Reactions in **Level 4** comprise the following :

1. Node 1 : CH_4 oxidation

   (a) $CH_4 + O_2 \rightarrow CO_2 + 2H_2$
   $\Delta G_{298K} = -343.73(kJ/mol)$
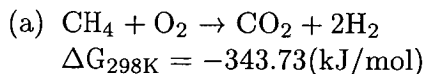
   Oxidation of methane produced carbon dioxide and hydrogen.

2. Node 2 : CO oxidation - phantom

3. Node 3 : oxidation of H_2 - phantom

4. Node 4 : $OHC_6H_4COCH_3$ - no new products

5. Node 5 : $OHC_6H_4CH_2OH$

   (a) $OHC_6H_4CH_2OH + O_2 \rightarrow H_2O + OHC_6H_4COOH$
   $\Delta G_{298K} = -435.89(kJ/mol)$
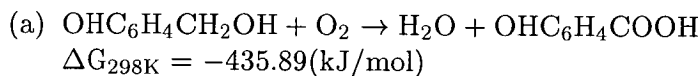
   One reaction was established from direct oxidation of p-hydroxy benzyl alcohol which produced H_2O and OHC_6H_4COOH. The reaction was generated by the transformation of the alcoholic bond to carboxylate. Both the program and the experimental studies showed the conversion of p-hydroxy benzyl alcohol directly into p-hydroxy benzoic. Theoretically, p-hydroxy benzaldehyde formation follows the transformation of alcohol, but it was not formed which was an indication of positive free energy change of reaction. This was probably due to the complex structure which prevented the formation of aldehyde from alcohol.

6. Node 6: oxidation of CH_3COCHO

   (a) $CH_3COCHO + H_2O \rightarrow H_2 + CH_3COCOOH$
   $\Delta G_{298K} = -15.59(kJ/mol)$
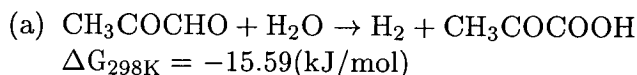
7. Node 7 : oxidation of $CHOCOCH=CHCOCHO$

   (a) $CHOCOCH=CHCOCHO + O_2 \rightarrow 2CHOCH=CHCHO + 2CO_2$
   $\Delta G_{298K} = -548.20(kJ/mol)$

   (b) $CHOCOCH=CHCOCHO + O_2 \rightarrow CO_2 + CHOCOCH=CHCOOH$
   $\Delta G_{298K} = -518.49(kJ/mol)$

   (c) $CHOCOCH=CHCOCHO + H_2O \rightarrow CHOCO[OH]CHCH_2COCHO$
   $\Delta G_{298K} = 9.32(kJ/mol)$
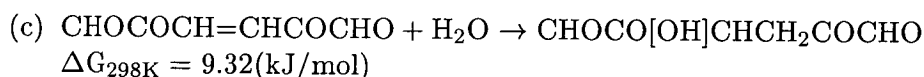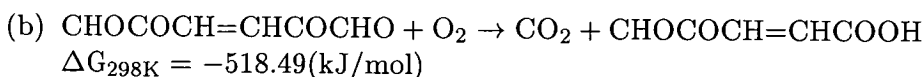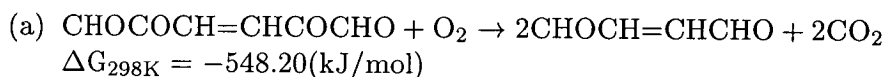
(d) $CHOCOCH=CHCOCHO + H_2O \rightarrow CHOCOCH_2[OH]CHCOCHO$
$\Delta G_{298K} = 9.32(kJ/mol)$

(e) $CHOCOCH=CHCOCHO + H_2O \rightarrow H_2 + CHOCOCH=CHCHO + CO_2$
$\Delta G_{298K} = -45.30(kJ/mol)$

(f) $CHOCOCH=CHCOCHO + H_2O \rightarrow H_2 + CHOCOCH=CHCOCOOH$
$\Delta G_{298K} = -15.59(kJ/mol)$

The above reactions produced 8 surviving species having had respective transformation of functional groups into other groups and also decarboxylation which reduces the number of carbon atoms. The reaction network in Devlin's mechanisms illustrated the pathways to produce short chain components which were obtained by double bond fissions and decarboxylations.

8. Node 8 : oxidation of $COOHCH=CHCH=CHCOOH$

(a) $COOHCH=CHCH=CHCOOH \rightarrow COOHCH=CHCH=CH_2 + CO_2$
$\Delta G_{298K} = -51.49(kJ/mol)$

(b) $COOHCH=CHCH=CHCOOH + O_2 \rightarrow CHOCOOH + COOHCH=CHCHO$
$\Delta G_{298K} = -330.14(kJ/mol)$

(c) $COOHCH=CHCH=CHCOOH + O_2 \rightarrow 2\ CO_2 + OHCH=CHCH=CHOH$
$\Delta G_{298K} = -391.86(kJ/mol)$

(d) $COOHCH=CHCH=CHCOOH + H_2O \rightarrow$
$COOHCH=CH[OH]CHCH_2COOH$
$\Delta G_{298K} = 9.32(kJ/mol)$

(e) $COOHCH=CHCH=CHCOOH + H_2O \rightarrow$
$COOHCH=CHCH_2[OH]CHCOOH$
$\Delta G_{298K} = 9.32(kJ/mol)$

(f) $COOHCH=CHCH=CHCOOH+H_2O \rightarrow H_2+OHCH=CHCH=CH_2+2\ CO_2$
$\Delta G_{298K} = -18.62(kJ/mol)$

9. Node 9: oxidation of $OHCH_2COCH=CHCOCHO$

(a) $OHCH_2COCH=CHCOCHO + O_2 \rightarrow H_2 + 2\ CHOCOCHO$
$\Delta G_{298K} = -292.84(kJ/mol)$

(b) $OHCH_2COCH=CHCOCHO + O_2 \rightarrow OHCH_2COCHO + CHOCOCHO$
$\Delta G_{298K} = -330.14(kJ/mol)$

(c) $OHCH_2COCH=CHCOCHO + H_2O \rightarrow OHCH_2CO[OH]CHCH_2COCHO$
$\Delta G_{298K} = 9.32(kJ/mol)$

The surviving species produced at this level consisted of intermediate species of aldehyde and ketone groups. Subsequent oxidation led to the formation of final experimentally observable components such as glyoxal, oxaloacetic acid, 3-oxo propanoic acid and malonic acid. These components can be seen at the end of the tree branch in the species tree diagram.

10. Node 10 : oxidation of $OHC_6H_4CH_2COOH$

(a) $OHC_6H_4CH_2COOH \rightarrow OHC_6H_4CH_3 + CO_2$
   $\Delta G_{298K} = -59.11(kJ/mol)$
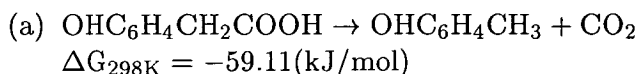
The above reaction was not observed in the experiment. This is due to the route to $OHC_6H_4CH_2COOH$ was not established. On the other hand, the route was constructed by the program which is from **Level 2 Node 4** through to **Level 3 Node 5.**

LEVEL 5

Level 5 and up involve generation of species having shorter chains. Chain reduction in oxidation reactions can be achieved by several ways, i.e :

- Decarboxylation which reduces the length of the chain by one atom carbon releasing carbon dioxide

- Double bond cleavage which splits a chain giving two different species depending on the location of the double bond

- Split of chain at ketone group

In diagram 4.3, the destruction of phenol to the ultimate products proceeded through two pathways, i.e. 2,5-dioxo-3-hexenedioic acid and muconic acid. Decarboxylation and acidification were carried out alternately during the process. The intermediate products consisted of species with 4 carbon atoms such as 1,4-dioxo-2-butene, 4-oxo-2-butenoic acid, maleic acid and succinic acid. These were followed by the formation of components with 3 carbon atoms namely propanoic acid, acrylic acid, 3-hydroxy-propanoic acid, 3-oxo-propanoic acid and malonic acid. Components with 2 carbon atoms generated from further reactions were glyoxal, glyoxilic acid, oxalic acid and acetic acid. These were finally broken down to formic acid and decomposed into carbon dioxide and water.

In the present work, decomposition performed through four pathways, that is :

- $OHCH_2COCH=CHCOCHO$

- CH_3COCHO

- $COOHCH=CHCH=CHCOOH$

- $CHOCOCH=CHCOCHO$

The structure of components of pathways 1 and 2 represented intermediate oxidation products in the form of alcohol, aldehyde and ketone. The oxidation of these components would give a similar structure to 2,5-dioxo-3-hexenedioic acid. Pathway 2 seemed to be less substantial since it was a direct cleavage product of phenol. This structure was obtained towards the end of the reaction. It can be seen that the results generated by this program for aromatic ring cleavage were consistent with that of the experimental studies. Cleavage products, such as $C_1 - C_4$ acids were found in

Mantzavinos work and formed through other routes.

Below are the detail of reactions in Level 5.

1. Node 1: oxidation of p-hydroxy-benzoic

   (a) $OHC_6H_4COOH \rightarrow OHC_6H_5 + CO_2$
       $\Delta G_{298K} = -49.48(kJ/mol)$
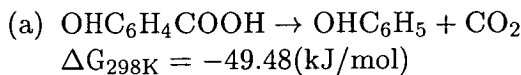
   Oxidation reaction on p-hydroxy-benzoic generated decarboxylated component producing phenol while releasing carbon dioxide.

2. Node 2 : oxidation of $OHC_6H_4CH_3$

   (a) $OHC_6H_4CH_3 + O_2 \rightarrow CHOCH=CHCH=CHCHO + CH_2O$
       $\Delta G_{298K} = -114.81(kJ/mol)$
   (b) $OHC_6H_4CH_3 + O_2 \rightarrow CH_2O + OHC_6H_4OH$
       $\Delta G_{298K} = -263.41(kJ/mol)$
   (c) $OHC_6H_4CH_3 + O_2 \rightarrow H_2 + CH_4 + CHOCOCH=CHCOCHO$
       $\Delta G_{298K} = -164.94(kJ/mol)$
   (d) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow H_2 + CH_2O + COOHCH=CHCH=CHCHO$
       $\Delta G_{298K} = -130.40(kJ/mol)$
   (e) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow CH_4 + COOHCH=CHCH=CHCOOH$
       $\Delta G_{298K} = -315.66(kJ/mol)$
   (f) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow CH_4 + OHCH_2COCH=CHCOCHO$
       $\Delta G_{298K} = -202.24(kJ/mol)$
   (g) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow CH_3OH + COOHCH=CHCH=CHCHO$
       $\Delta G_{298K} = -199.68(kJ/mol)$
   (h) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow OHCH=CHCH=CHCH_2OH + CH_2O + CHOCHO$
       $\Delta G_{298K} = -66.09(kJ/mol)$
   (i) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow OHCH=CH_2 + CHOCHO + CHOCH=CH_2$
       $\Delta G_{298K} = -90.45(kJ/mol)$
   (j) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow CH_2O + CHOCH=CH_2 + CH_3COCHO$
       $\Delta G_{298K} = -138.41(kJ/mol)$
   (k) $OHC_6H_4CH_3 + O_2 + H_2O \rightarrow CH_3COCHO + OHCH=CHCH=CHOH$
       $\Delta G_{298K} = -121.51(kJ/mol)$

   The program generated this node, which was not found in the experiments. At this stage, oxidation destabilized the aromatic ring and thus led to ring destruction. Species generated by the opening of the aromatic ring were muconic acid, 2,5-dioxo-3-hexenedial and so on.

3. Node 4 : $CHOCO[OH]CHCH_2COCHO$

   (a) $CHOCO[OH]CHCH_2COCHO \rightarrow H_2 + CHOCOCOCH_2COCHO$
       $\Delta G_{298K} = -10.34(kJ/mol)$

(b) $2CHOCO[OH]CHCH_2COCHO \rightarrow CHOCOCH_2OH + CH_3COCHO + CHOCOCOCH_2COCHO$
$\Delta G_{298K} = -38.10(kJ/mol)$

(c) $2CHOCO[OH]CHCH_2COCHO \rightarrow CHOCHO + OHCH_2CH_2COCHO + CHOCOCOCH_2COCHO$
$\Delta G_{298K} = -8.70(kJ/mol)$

(d) $CHOCO[OH]CHCH_2COCHO \rightarrow H_2 + CHOCO[OH]CHCH_2COCOOH$
$\Delta G_{298K} = -15.59(kJ/mol)$

(e) $CHOCO[OH]CHCH_2COCHO \rightarrow OHCH_2CH_2COCHO + CHOCOOH$
$\Delta G_{298K} = -34.63(kJ/mol)$
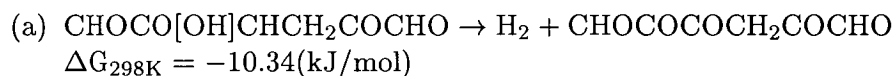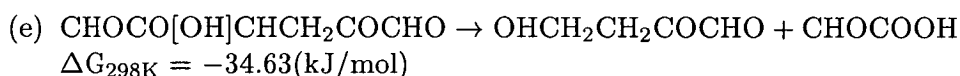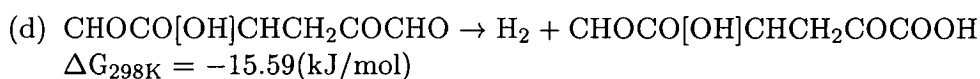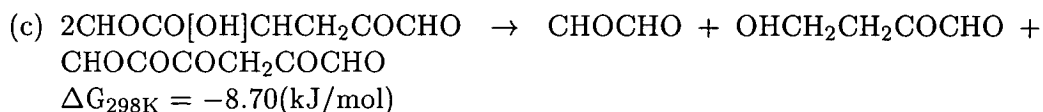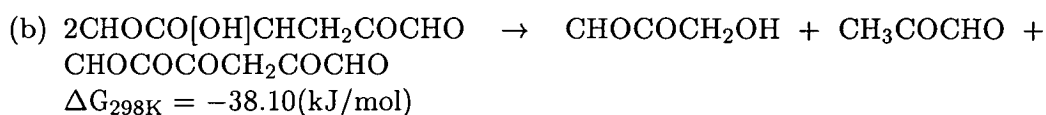
4. Node 5 : $CHOCOCH=CHCOCOOH$

(a) $CHOCOCH=CHCOCOOH + H_2O \rightarrow H_2 + COOHCOCH=CHCOCOOH$
$\Delta G_{298K} = -15.59(kJ/mol)$
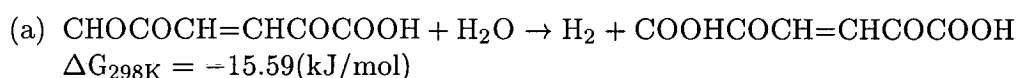
5. Node 6 : oxidation of C_6H_5OH

(a) $OHC_6H_5 + O2 \rightarrow COOHCH=CHCH=CHCHO$
$\Delta G_{298K} = -250.41(kJ/mol)$

(b) $OHC_6H_5 + O2 + H_2O \rightarrow H_2 + COOHCH=CHCH=CHCOOH$
$\Delta G_{298K} = -266.00(kJ/mol)$

(c) $OHC_6H_5 + O2 + H_2O \rightarrow H_2 + OHCH_2COCH=CHCOCHO$
$\Delta G_{298K} = -152.58(kJ/mol)$

(d) $OHC_6H_5 + O2 + H_2O \rightarrow 2CH_3COCHO$
$\Delta G_{298K} = -246.38(kJ/mol)$
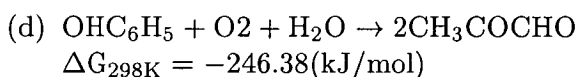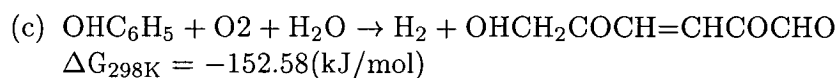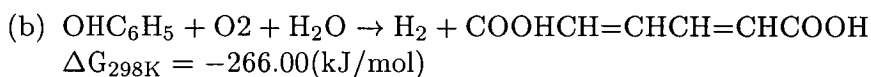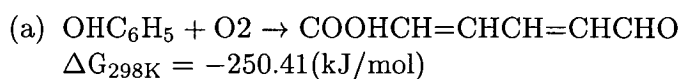
The oxidation of phenol caused the aromatic ring to break forming a straight chain with diacid and double bonds. Similar results were found in the reaction network of the experimental work where aromatic ring fracture was observed at this stage.

6. Node 7 : oxidation of $COOHCH=CHCH=CHCHO$

(a) $COOHCH=CHCH=CHCHO + H_2O \rightarrow H_2 + COOHCH=CHCH=CHCOOH$
$\Delta G_{298K} = -15.59(kJ/mol)$
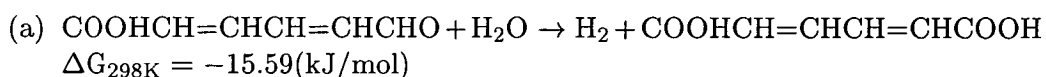
The reaction generated the following component : $COOHCH=CHCH=CHCOOH$ (2,5-dioxo-3-hexenedioic acid) and H_2. It was constructed by oxidizing the aldehyde to form carboxylate.

Surviving species generated at this level represented intermediates which later converted into refractory intermediates in the form of acids as mentioned above. These materials can be seen towards the end of the branch of the species tree.

Many other compounds as seen in the tree such as $CH_3CH=CHCHO$ and CH_3COCHO were not mentioned in other publication. These compounds were generated through

routes which were not generated during the experiments. The generation of certain routes is probably due to the thermodynamic selectivity, where reactions occur toward those with the highest negative free energy change. Thus, theoretically feasible reactions would be generated by the program, but not during experiments.

Since duplication was eliminated from the diagram, further expansions of certain species were not shown.
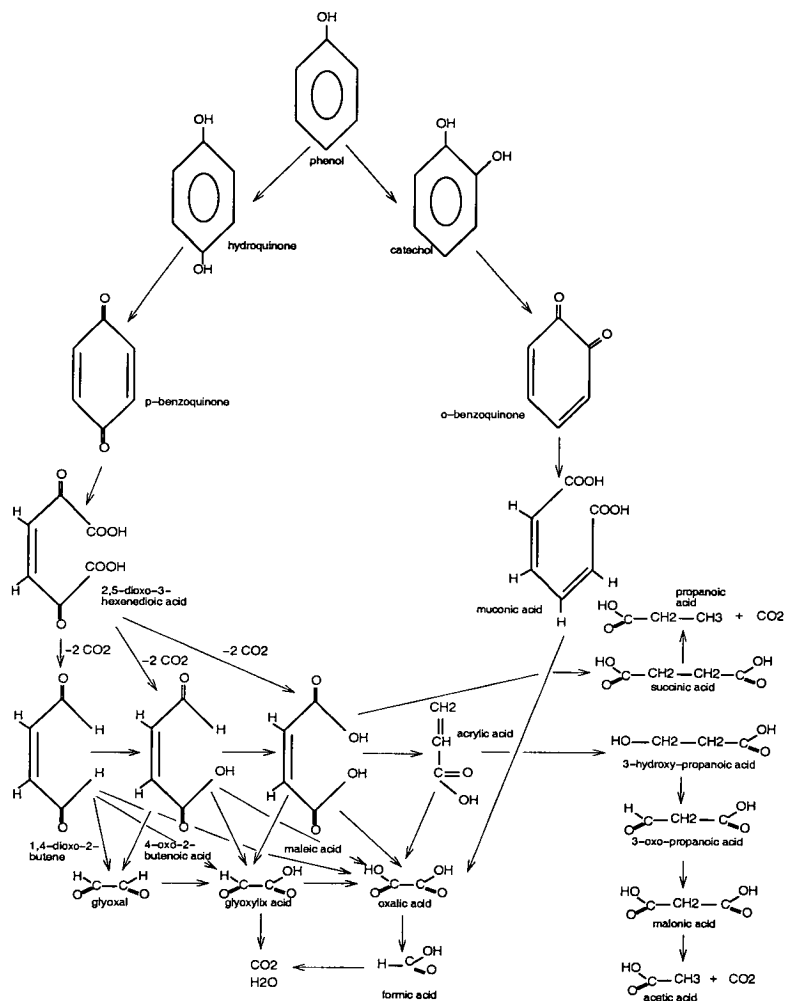
Figure 4.3: Reaction network for aqueous phenol destruction[45]

4.3.2 Alkylation of toluene with ethanol

The alkylation reaction of toluene was chosen due to the occurence of many side reactions, which are of interest because some of them are harmful to the catalyst. The main product of the alkylation is p-ethyltoluene ($CH_3CH_2C_6H_4CH_3$), but there are also a number of other substituted compounds. The products of ethyltoluene isomers are significant for obtaining p-methylstyrene which is the monomer for poly (4-methyl styrene). p-methylstyrene is a result of dehydrogenation of p-ethyltoluene.

Alkylation reaction involves electrophilic aromatic substitution which is the substitution of hydrogen in toluene by an alkyl group. Radicals are produced by hydrogen abstraction from toluene and 'OH' group and fragmentation of alcohol into alkyl groups, dehydration and dehydrogenation of alcohols. Typical reaction of radicals in the alkylation of toluene is substitution and disproportionation[51, 52]. In the experimental work, the reactions were carried out at the temperature of 623 to 673 K.

The experimental studies done by Walendziewski[44], Lonyi[51] and Paparatto[52] were concerned with the application of catalysts to increase the selectivity of the main product (para-ethyl toluene). This work focussed on generating alkyl substituted products while suppressing other substituted byproducts such as alcohols. The reaction network was not established, the comparison was based on the number of products generated during the experiments and that generated by the program. It was found that all components found in the experiments can be generated by the program. Other components of alcohol, aldehyde, olefins, ketone and ether groups were also generated, but these components were not found in the experimental studies. Below is the mechanisms of the substitution reaction during species generation at **Level 1** and **Level 2**.

LEVEL 1

Level 1 involved reactions between the starting species. In the present work, toluene is represented as $C_6H_5CH_3$ and ethanol as CH_3CH_2OH. Isomer products of some aromatic derivatives such as m-xylene or o-xylene are not distinguished from p-xylene, as functional group position does not effect the value of group properties. The types of functional group remain the same in these derivatives, while it is not the case in straight aliphatic chain where the properties of isomers are different from that of normal chain.

Radicals generated from toluene and ethanol are as follows: $\dot{C}_6H_4CH_3$, $C_6H_5\dot{C}H_2$, $\dot{C}_6H_5$, $\dot{C}H_3$, $CH_3\dot{C}H_2$, $\dot{H}$, $\dot{C}H_2\dot{C}H_2$, $CH_3\dot{C}H$ and $\dot{O}H$. The combinations of these radicals produce $CH_3CH_2C_6H_4CH_3$, $C_6H_5CH_2CH_3$, $CH_3C_6H_4CH_3$, $CH_3CH_2CH_3$ and so on. The detail of the reactions are shown below.

```
Number of reactants      2
C6H5CH3
CH3CH2OH
```

Radicals of component   C6H5CH3   5

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	C6H5CH2	-1	F	1	0
3	C6H4CH3	-1	T	2	0
4	CH3	-1	T	1	0
5	C6H5	-1	F	1	0

Radicals of component   CH3CH2OH   8

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	OH	-1	T	1	0
2	CH3CH2	-1	F	1	0
3	CH2OH	-1	T	2	0
4	CH3	-1	F	1	0
5	H	-1	T	1	0
6	CH3CH2O	-1	F	1	0
7	CH3CH	-2	F	1	1
8	CH2CH2	-2	F	1	2

```
New products             37
            1    H2O
            2    CH3CHO
            3    CH3CH3
            4    CH3OH
            5    CH4
            6    H2
            7    CH3CH2OH
            8    CH2:CH2:
            9    {ch2ch2ch2ch2}
           10    CH3CH2CH2C6H5
           11    C6H5CH2CH2OH
           12    CH3CH2C6H5
           13    C6H5CH3
           14    CH3CH2OCH2C6H5
           15    CH3CH2C6H4CH3
           16    OHCH2C6H4CH3
           17    CH3C6H4CH3
           18    CH3CH2OC6H4CH3
           19    CH3CH2CH3
           20    CH3CH2OCH3
           21    CH3[CH3]CHCH3
           22    CH3CH2CH2CH3
```

23	C6H5CH2OH
24	C6H6
25	CH3CH2OC6H5
26	CH3[C6H5]CHC6H5
27	C6H5CH2CH2C6H5
28	C6H5CH2C6H4CH3
29	C6H5CH2C6H5
30	CH3C6H4C6H4CH3
31	C6H5C6H5
32	CH3CH2CH2OH
33	CH3CH2OCH2CH3
34	OHCH2CH2OH
35	CH3CH2OCH2OH
36	CH3CH2CH2CH2CH3
37	CH3CH2CH2CH2OH

At **Level 1**, the combinations of the radicals were able to generate 37 possible new species. These species were generated from 15 stoichiometrically feasible reactions producing 18 surviving species. The following are the reactions obtained from the first level.

1. $2\ C_6H_5CH_3 \rightarrow CH_4 + C_6H_5CH_2C_6H_5$
   $\Delta G_{298K} = -8.41$ (kJ/mol)

2. $2\ C_6H_5CH_3 \rightarrow CH_3CH_2C_6H_5 + C_6H_6$
   $\Delta G_{298K} = 9.63$ (kJ/mol)

3. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3CHO + CH_3CH_3$
   $\Delta G_{298K} = -54.68$ (kJ/mol)

4. $CH_3CH_2OH \rightarrow H_2O + CH_2{=}CH_2$
   $\Delta G_{298K} = 3.48$ (kJ/mol)

5. $2\ CH_3CH_2OH \rightarrow 2\ H_2O + C_4H_8$
   $\Delta G_{298K} = -76.72$ (kJ/mol)

6. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3CH_2OCH_2CH_3$
   $\Delta G_{298K} = -9.28$ (kJ/mol)

7. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3CH_2CH_2CH_2OH$
   $\Delta G_{298K} = -41.10$ (kJ/mol)

8. $2\ CH_3CH_2OH \rightarrow CH_3CHO + CH_3OH + CH_4$
   $\Delta G_{298K} = -21.99$ (kJ/mol)

9. $C_6H_5 + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2CH_2C_6H_5$
   $\Delta G_{298K} = -41.10$ (kJ/mol)

10. $C_6H_5 + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2C_6H_4CH_3$
    $\Delta G_{298K} = -50.73$ (kJ/mol)

11. $C_6H_5 + CH_3CH_2OH \rightarrow CH_3CHO + CH_4 + C_6H_6$
    $\Delta G_{298K} = -12.36$ (kJ/mol)

12. $C_6H_5 + CH_3CH_2OH \rightarrow CH_3OH + CH_3C_6H_4CH_3$
    $\Delta G_{298K} = -9.63$ (kJ/mol)

13. $C_6H_5CH_3 + CH_3CH_2OH \rightarrow CH_4 + C_6H_5CH_2CH_2OH$
    $\Delta G_{298K} = -8.41$ (kJ/mol)

14. $C_6H_5CH_3 + CH_3CH_2OH \rightarrow CH_4 + OHCH_2C_6H_4CH_3$
    $\Delta G_{298K} = -18.04$ (kJ/mol)

15. $C_6H_5CH_3 + CH_3CH_2OH \rightarrow C_6H_6 + CH_3CH_2CH_2OH$
    $\Delta G_{700K} = 9.63$ (kJ/mol)

The following is the list of the surviving species at **Level 1** :
CH_4, $C_6H_5CH_2C_6H_5$, $CH_3CH_2C_6H_5$, C_6H_6, CH_3OH, $CH_3C_6H_4CH_3$, $C_6H_5CH_2CH_2OH$, $OHCH_2C_6H_4CH_3$, $CH_3CH_2CH_2OH$, H_2, $CH_2=CH_2$, C_4H_8, $CH_3CH_2CH_2C_6H_5$, $CH_3CH_2C_6H_4CH_3$, CH_3CHO, CH_3CH_3, $CH_3CH_2OCH_2CH_3$, and $CH_3CH_2CH_2C_6H_5$. p-ethyl toluene has been generated at this stage, as a result of substitution reaction of methyl toluene. See components in **Level 2** for further substitution of p-ethyl toluene. The complete results are shown in Figure 4.4.

In the experimental study, the individual chemicals found in the products ranged from 12 to 38 compounds besides the desired product, p-ethyltoluene. Table 4.1 provides the major compounds found in the liquid products[44].

Table 4.1: Chemical compounds found in the products of the alkylation of toluene

ethanol	ethyl ether	heptane
benzene	toluene	ethyl benzene
p-xylene	1-ethyl-3-methylbenzene	1-ethyl-4-methylbenzene
1-ethyl-2-methylbenzene	trimethylbenzene	methylisopropylbenzene
diethylbenzene	methylpropylbenzene	ethyldimethylbenzene
1,3-diethyl-5-methylbenzene	2,4-diethyl-1-methylbenzene	diethylmethylbenzene
1,4-diethyl-2-methylbenzene	triethylbenzene	dimethyldiethylbenzene
triethylmethylbenzene	tetraethylbenzene	ethylmethylbenzene
other polysubstituted products		

The number of products obtained in the experiments depends on the selected catalysts since the objective of the experiments was to investigate the performance of the catalysts. Side reaction formation was suppressed by using shape-selective properties of catalysts or introducing inorganic additives[51, 52]. However, the selectivity of the catalysts will not be discussed here.

It was found that components identified in the above experimental studies can be generated by the program. However, the tree diagram also contained a considerable number of species which were not mentioned in the publications, although it was reported that carbonaceous deposits could form and deactivate the catalysts. As it has been mentioned that the experimental work dealt with the investigation of catalyst performance in the alkylation of toluene with ethanol, the catalysts were selected to work on improving the selectivity of alkyl substitution. Therefore, the formation of other undesired species and alcohols were suppressed.

LEVEL 2

Level 2 and up involved further substitution reaction of the aromatic hydrogen. An example is shown using the expansion of $CH_3CH_2C_6H_4CH_3$ (p-ethyl toluene).

```
Number of reactants       2
CH3CH2C6H4CH3
CH3CH2OH
```

Radicals of component   CH3CH2C6H4CH3   8

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	CH3CH2C6H4CH2	-1	F	1	0
3	CH3CH2C6H3CH3	-1	F	2	0
4	CH3	-1	T	1	0
5	CH3CH2C6H4	-1	F	1	0
6	C6H4CH3	-1	T	2	0
7	CH3CH2	-1	F	1	0
8	CH2C6H4CH3	-1	T	3	0

Radicals of component   CH3CH2OH   8

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	OH	-1	T	1	0
2	CH3CH2	-1	F	1	0
3	CH2OH	-1	T	2	0
4	CH3	-1	F	1	0
5	H	-1	T	1	0
6	CH3CH2O	-1	F	1	0
7	CH3CH	-2	F	1	1
8	CH2CH2	-2	F	1	2

```
New products             43
              1      H2O
              2      CH3CHO
              3      CH3CH3
              4      CH3OH
```

5	CH4
6	H2
7	CH3CH2OH
8	CH2:CH2:
9	{ch2ch2ch2ch2}
10	CH3CH2CH2C6H4CH2CH3
11	CH3CH2C6H4CH2CH3
12	CH3CH2C6H4CH3
13	CH3CH2[CH3CH2]C6H3CH3
14	CH3CH2[CH3]C6H3CH3
15	CH3CH2CH3
16	CH3CH2OCH3
17	CH3[CH3]CHCH3
18	CH3CH2CH2CH3
19	CH3CH2C6H4CH2OH
20	CH3CH2C6H5
21	OHCH2C6H4CH3
22	CH3C6H4CH3
23	C6H5CH3
24	CH3CH2OC6H4CH3
25	CH3CH2CH2OH
26	CH3CH2OCH2CH3
27	CH3CH2C6H4C6H4CH3
28	CH3C6H4C6H4CH3
29	CH3C6H4CH2C6H4CH3
30	CH3CH2CH2C6H4CH3
31	OHCH2CH2OH
32	CH3CH2OCH2OH
33	CH3CH2OOCH2CH3
34	CH3[CH3]CHCH2CH3
35	CH3[CH3]CHCH2OH
36	CH3[CH3CH2]CHCH3
37	CH3[OHCH2]CHCH3
38	CH3CH2CH2CH2CH2CH3
39	OHCH2CH2CH2CH2CH3
40	CH3CH2CH2CH2CH3
41	OHCH2CH2CH2CH2OH
42	CH3CH2CH2CH2OH
43	CH3CH2OCH2CH2CH3

There were 43 new species generated and the reactions established from p-ethyl toluene and ethanol are set out below :

1. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow C_4H_8 + 2\ C_6H_5CH_3$
   $\Delta G_{298K} = 9.63 (kJ/mol)$

2. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow CH_3CH_2CH_2C_6H_4CH_2CH_3 + CH_3C_6H_5$
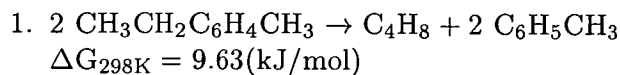
$$\Delta G_{298K} = 9.63(kJ/mol)$$

3. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow CH_3CH_2C_6H_4CH_2CH_3 + CH_3CH_2C_6H_5$
$$\Delta G_{298K} = 9.63(kJ/mol)$$

4. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow CH_3CH_2[CH_3]C_6H_3CH_3 + CH_3C_6H_4CH_3$
$$\Delta G_{298K} = -9.63(kJ/mol)$$

5. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow CH_3[CH_3]CH_3 + CH_3C_6H_4C_6H_4CH_3$
$$\Delta G_{298K} = -2.44(kJ/mol)$$

6. $2\ CH_3CH_2C_6H_4CH_3 \rightarrow CH_3CH_2C_6H_5 + CH_3CH_2CH_2C_6H_4CH_3$
$$\Delta G_{298K} = 9.63(kJ/mol)$$

7. $CH_3CH_2OH \rightarrow H_2O + CH_2{=}CH_2$
$$\Delta G_{298K} = 3.48(kJ/mol)$$

8. $2\ CH_3CH_2OH \rightarrow 2\ H_2O + C_4H_8$
$$\Delta G_{298K} = -76.72(kJ/mol)$$

9. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3CH_2OCH_2CH_3$
$$\Delta G_{298K} = -9.28(kJ/mol)$$

10. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3[CH_3]CHCH_2OH$
$$\Delta G_{298K} = -43.54(kJ/mol)$$

11. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3[OHCH_2]CHCH_3$
$$\Delta G_{298K} = -43.54(kJ/mol)$$

12. $2\ CH_3CH_2OH \rightarrow H_2O + CH_3CH_2CH_2CH_2OH$
$$\Delta G_{298K} = -41.10(kJ/mol)$$

13. $2\ CH_3CH_2OH \rightarrow CH_3CHO + CH_3OH + CH_4$
$$\Delta G_{298K} = -21.99(kJ/mol)$$

14. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow H_2O + 2\ CH_2{=}CH_2 + C_6H_5CH_3$
$$\Delta G_{298K} = -3.34(kJ/mol)$$

15. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow H_2O + 2\ C_4H_8 + C_6H_5CH_3$
$$\Delta G_{298K} = -25.99(kJ/mol)$$

16. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2CH_2C_6H_4CH_2CH_3$
$$\Delta G_{298K} = -41.10(kJ/mol)$$

17. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow H_2O + CH_3CH_2[CH_3CH_2]C_6H_3CH_3$
$$\Delta G_{298K} = -50.73(kJ/mol)$$

18. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow CH_3CHO + CH_3CH_3 + C_6H_5CH_3$
$$\Delta G_{298K} = -3.95(kJ/mol)$$

19. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow CH_3CHO + CH_4 + CH_3CH_2C_6H_5$
$$\Delta G_{298K} = -12.36(kJ/mol)$$

20. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow CH_3CHO + CH_4 + CH_3C_6H_4CH_3$
$$\Delta G_{298K} = -21.99(kJ/mol)$$

21. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow CH_3OH + CH_3CH_2[CH_3]C_6H_3CH_3$
$\Delta G_{298K} = -9.63(kJ/mol)$

22. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow CH_3CH_2C_6H_5 + CH_3CH_2CH_2OH$
$\Delta G_{298K} = 9.63(kJ/mol)$

23. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow C_6H_5CH_3 + CH_3[CH_3]CHCH_2OH$
$\Delta G_{298K} = 7.19(kJ/mol)$

24. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow C_6H_5CH_3 + CH_3[OHCH_2]CHCH_3$
$\Delta G_{298K} = 7.19(kJ/mol)$

25. $CH_3CH_2C_6H_4CH_3 + CH_3CH_2OH \rightarrow C_6H_5CH_3 + CH_3CH_2CH_2CH_2OH$
$\Delta G_{298K} = 9.63(kJ/mol)$

The above reactions produced 22 surviving species :
C_4H_8, $C_6H_5CH_3$, $CH_3CH_2CH_2C_6H_4CH_2CH_3$, $CH_3CH_2C_6H_4CH_2CH_3$, $CH_3CH_2C_6H_5$, $CH_3CH_2[CH_3]C_6H_3CH_3$, $CH_3C_6H_4CH_3$, $CH_3[CH_3]CHCH_3$, $CH_3C_6H_4C_6H_4CH_3$, $CH_3CH_2CH_2C_6H_4CH_3$, H_2O, CH_3CHO, CH_3CH_3, $CH_2=CH_2$, $CH_3CH_2OCH_2CH_3$, $CH_3[CH_3]CHCH_2OH$, $CH_3[OHCH_2]CHCH_3$, $CH_3CH_2CH_2CH_2OH$, CH_3OH, CH_4, $CH_3CH_2[CH_3CH_2]C_6H_3CH_3$, and $CH_3CH_2CH_2OH$.

From these reactions, it can be seen that further substitution led to the formation of ethyl toluene. Other substituted compounds, aldehyde, olefin and ether compounds were also formed. The next levels generated 1-ethyl-3-methylbenzene, 1-ethyl-4-methylbenzene, 1-ethyl-2-methylbenzene, trimethylbenzene and methylisopropylbenzene.
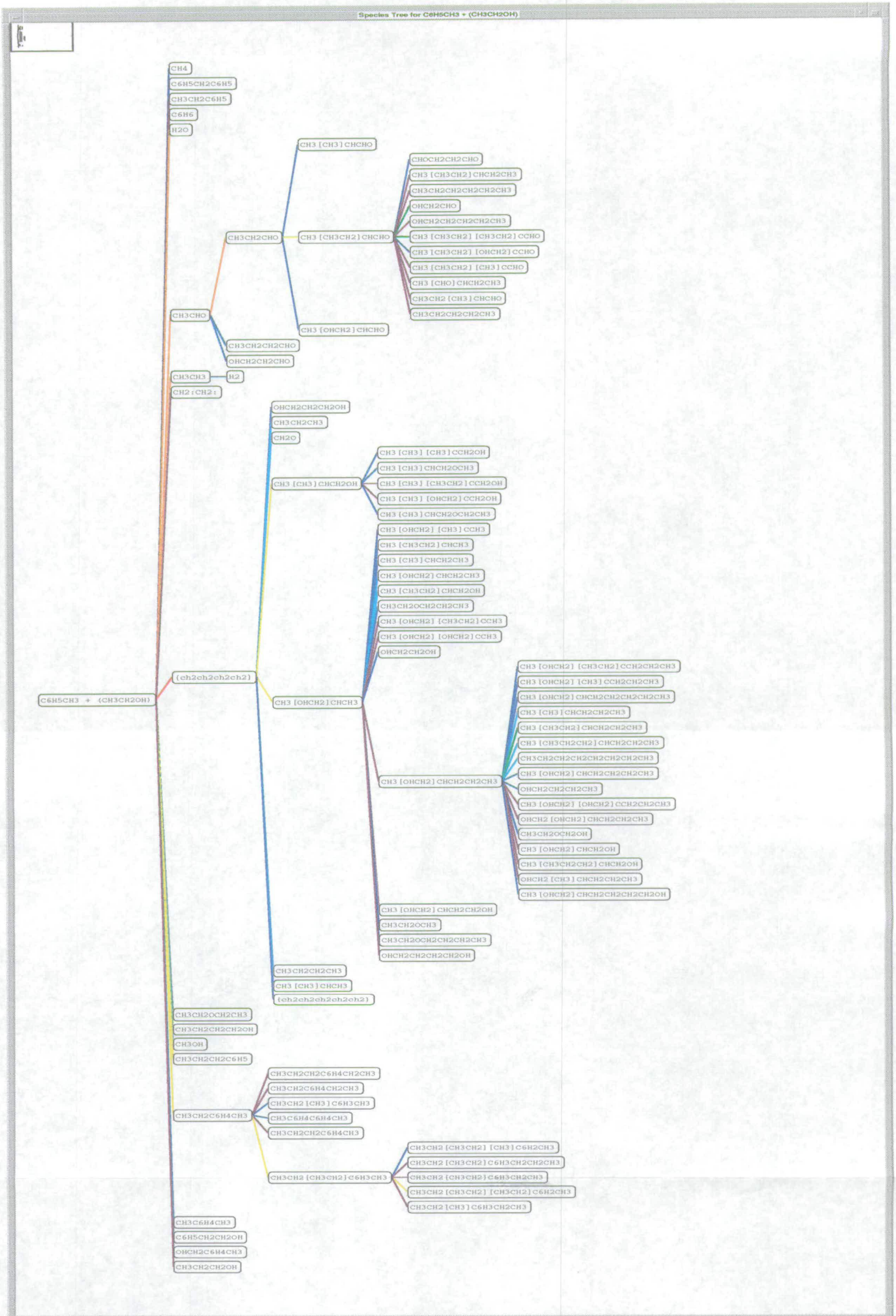
Figure 4.4: Graphical view of node expansion of the alkylation of toluene

4.3.3   Sensitivity Analysis

Sensitivity analysis is concerned with the investigation of possible species generation in relation to the value of free energy changes and temperature. There is a threshold value associated with free energy changes to determine process feasibility. Therefore, free energy changes can be used as 'tuning parameter' for the method used in this task. The correlation of free energy changes and the number of feasible reactions has been studied and the results are presented below.

The study on the threshold values of free energy changes has been accomplished using wet oxidation reaction of coumaric acid. Slightly different networks have been obtained as a result of applying four different values of the tuning parameter, i.e. strictly negative, maximum 10 kJ/mol, maximum 40 kJ/mol and negative but having a wider temperature bound (298 - 1500 K). Figure 4.5 shows the reaction network of strictly negative free energy change with tight bound. Tight bound refers to negative free energy change with moderate reaction condition having the temperature below 500 K which is usually used in experimental condition. It shows that at **Level 1**, four species were generated providing two reaction paths.

At **Level 2**, the oxidation of p-hydroxy-benzaldehyde generates four new species, while the oxidation of p-vinyl phenol does not generate any new species since the addition of OH group to the structure gives a positive free energy change. Therefore, this network does not produce a reaction path containing the sequence of p-hydroxy-benzal-alcohol and p-hydroxy benzoic acid. As for the opening of aromatic ring, which requires negative free energy change, the paths generated follows the main route as presented by Devlin.

The use of free energy change of 10 kJ/mol has been discussed in section 4.3.1. The network displays more components compared to that of the strictly negative free energy change. This network features a very similar result to that of the experimental work, although there are a few species which were not found in the experiments. If both free energy changes and temperature bound are relaxed, more components can be generated. The reaction network produced by using free energy change of 40 kJ/mol is shown in Figure 4.6. There are several more components generated by the increasing free energy change threshold value such as : $OHC_6H_4CH=CHOH$ which was obtained at $\Delta G_{298} = 32.87 kJ/mol$). Previously infeasible reaction such as the transformation of alcohol into aldehyde as shown below may occur :

$CHOCH_2OH \rightarrow H_2 + CHOCHO$
$\Delta G_{298} = 37.30 kJ/mol$
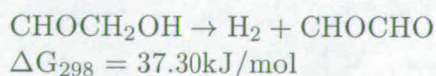
The application of negative free energy change within a wider temperature range (298 - 1500 K) is shown in Figure 4.7. Similar component to above was produced at high temperature, i.e 600 K with negative ΔG_{298} equal to -2.27 kJ/mol. The generation of component such as $(OH)(OH)C_6H_3CH=CH_2$ was possible when the reaction temperature is sufficiently high, i.e. 1100 K. This reaction is not found under previous conditions. Some fragmentation and decomposition reactions may also be found at
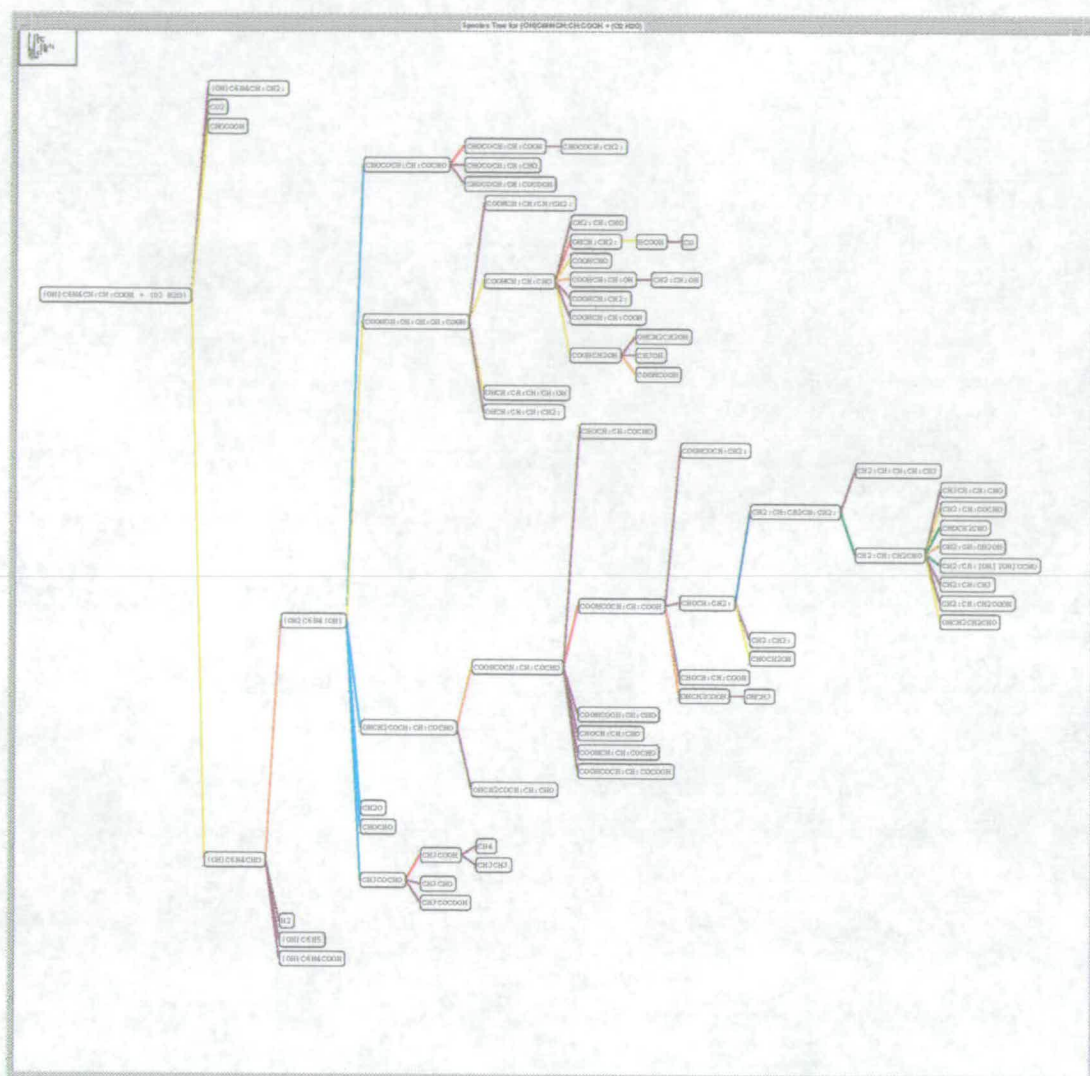
Figure 4.5: Products for p-coumaric acid based on strictly negative free energy change

higher temperature.

- $OHC_6H_4CH=CH_2 + H_2O \rightarrow (OH)(OH)C_6H_3CH=CH_2$
  $\Delta G_{1100} = -1.46 kJ/mol$

- $COOHCOCOCOCHO + H_2O \rightarrow O_2 + 5CO + 2H_2$
  $\Delta G_{800} = -12.31 kJ/mol$

The results of the above study shows that there is a relationship between the number of species generated and the threshold values of free energy changes and range of reaction temperature. More probabilities can be discovered if the values of both parameters are relaxed. However, the number of new species generated are not excessively large, there is only a slight difference in the species tree diagram. Most reactions occur at negative free energy changes and moderate conditions. Therefore, in the study of coumaric acid
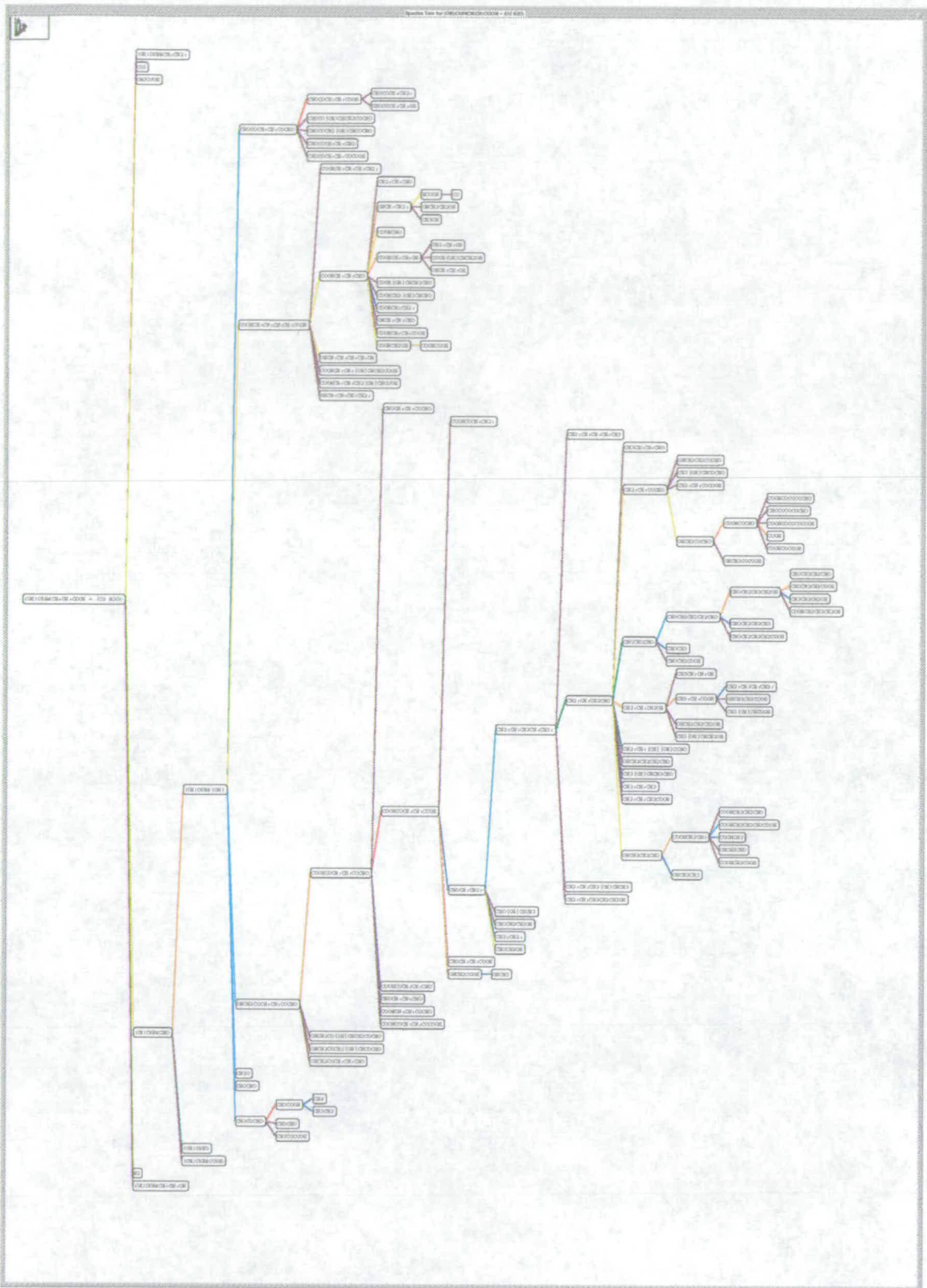
Figure 4.6: Reactions based on maximum free energy change of 40 kJ/mol
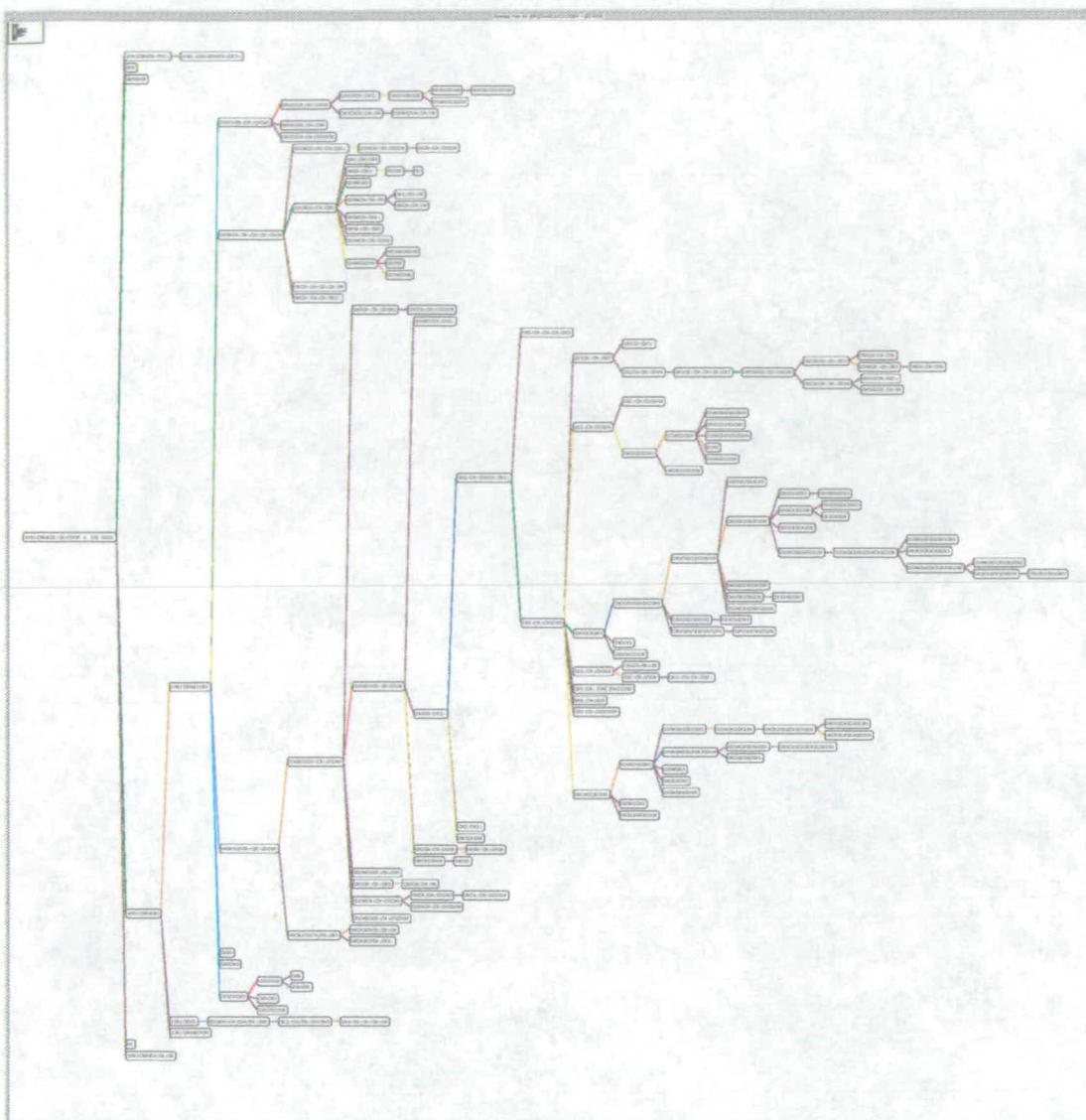
Figure 4.7: Reactions based on negative free energy changes within 298 - 1500 K temperature range

the most feasible threshold value is small positive free energy change, i.e 10 kJ/mol. However, this does not restrict the use of slightly higher (40 kJ/mol) since the entire results do not present significance difference. Certain components were generated by the program for having negative free energy changes, while they were not found in the experiments.

The applicability of small positive free energy changes may also be justified by examining the accuracy of Joback group contribution technique. A comparative study on the estimation and literature values for a variety of components has been done and shown a variation of differences ranging from 1 to 74. However, most components lie in the range of 20 - 30. The differences depend largely on the chemical structures as

can be seen in Table D.1 and Figures D-1 and D-2 in Appendix D. Simple alkane structure can be expected to be more accurate, while more complicated halogenanized components or components having cyclic structure are less accurate. Hence, a value of 10 kJ/mol is considered within the range of error.

Since temperature corresponds with free energy changes, a few components have been chosen to demonstrate the relative values. See the diagram of the temperature effect in Appendix D for ethane, $ClCH_2CHO$, $ClCH=CCl_2$, CH_3CH_2F and $CH_2=CHCl$. The effect of the temperature is exponential, at low and medium temperature level (up to 600 K) the curve is rather flat, but it descends quite sharply when the temperature is raised above 600 K. The five components show similar behaviour, although the structure of the components are very different. Therefore, this illustration confirms that molecular properties change when the condition is changed.

4.3.4 Results of the Program Run Times

The program was run on SUN SPARC Ultra Machine using UNIX Solaris 2.6 operating system. The duration varied depending on the number of initial species, the number of nodes expanded and the number of new species generated. To run coumaric acid reactions having 3 initial species and 100 nodes to expand took about 35 minutes to complete. An alkylation reaction which has 2 initial species and 80 nodes to expand required 90 minutes to accomplished.

The largest memory consumer in the program is Program *React* which used a combinatorial approach to generate reactions. Therefore, if the number of initial species increased or the number of new species generated increased, then it takes longer for the program to accomplish the task. The number of new species in coumaric acid reactions was much less than the number of new species in alkylation reactions. So, the run time to process coumaric acid reactions was also less.

4.3.5 Summary

From the results above, it can be seen that generating new species by random combination of radicals must be augmented by using general rules of fundamental chemistry. Hence, knowledge of the chemistry could be crucial. The random combinatorial approach used in finding the feasible reactions can generate any type of reaction without referring to structural restrictions. Experience shows that negative free energy changes can be obtained as a result of the summation of several reactions. Therefore, in order to ensure the robustness of the procedures, slightly loose interpretation of chemistry principles is incorporated. In the case of coumaric acid oxidation, this is done by emulating the mechanisms of oxidation reaction on the functional groups building the chemical compound. As a result, the actual pathways of the chemical reactions can be produced. The study on coumaric acid shows that the number of reaction pathways generated by the program is similar to that of the experiments. Both the programs and the experiments could generate two reaction routes.

From the free energy changes point of view, although the preliminary study indicates that the maximum value of 40 kJ/mol is acceptable, but it may not be widely applicable. Therefore, it seems that an absolute maximum cannot be acquired. Some systems may need absolutely negative free energy changes, while others require slightly positive. The comparative study of coumaric acid oxidation suggested that 40 kJ/mol does not give significant difference. However, if the value is reduced to 10 kJ/mol, different results will be obtained as to which less number of species was generated. The program was able to generate two reaction routes which was in agreement with the experiments, while there were three routes generated using the maximum free energy change of 40 kJ/mol.

As a conclusion, the condition of plausibility may be varied according to the type of the system being examined. The sensitivity study shows that small positive free energy change under moderate condition appears to be sensible for feasibility evaluation. This can be also be justified upon the examination of Joback group contribution technique, where the difference between the literature data and the estimation is 20-30 kJ/mol. The application of 10 kJ/mol is within the range of error. The moderate condition is chosen due to normal reaction condition found in experimental work or industries.

From the comparison of the Joback method and the literature data to estimate the free energy values, the large discrepancy of some components indicates that Joback method is inaccurate. Joback derived his group contribution using the values given in Stull[53] to calculate the enthalpy, free energy and heat capacity polynomial coefficients while retaining the same molecular and atomic group as in critical property estimation. This may contribute to the inaccuracy of the Joback technique where chemical thermodynamics cannot be represented by simplified functional groups.

Chapter 5

Studies on Side Reaction Generation in Identified Processes

5.1 Introduction

This chapter demonstrates the application of the program to some industrial processes to investigate side reaction accumulation. The study involves separation simulation, where the separability of product components based on their volatilities were determined. Components having close boiling points may be difficult to separate. So, their continuous presence in the process line was suspected. A substantial number of undesirable components may accumulate through the recycles. It is therefore essential to have knowledge on possible side reactions and the effect of prevailing traces in the system. Studies on side reactions in chemical plants are illustrated using the vinyl chloride monomer, R-134a (1,1,1,2-tetrafluoroethane) and R-22 (chlorodifluoromethane) processes.

5.2 The Vinyl Chloride Monomer Process

5.2.1 Introduction

Vinyl chloride monomer is manufactured via ethylene dichloride (EDC)[54, 58] through the so-called 'balanced oxychlorination process'. The formation of byproducts has been investigated in the vinyl chloride monomer process, using the method described in the previous chapter. Many of the species found have boiling points close to that of EDC from which they must be separated before entering the pyrolysis reactor. They also tend to form non ideal mixtures, making their complete separation from EDC difficult. These would be expected to accumulate in the two process recycles. The purification of EDC in two large distillation columns has also been modelled. Figure 5.1 illustrates the lay out of the process[54, 58].
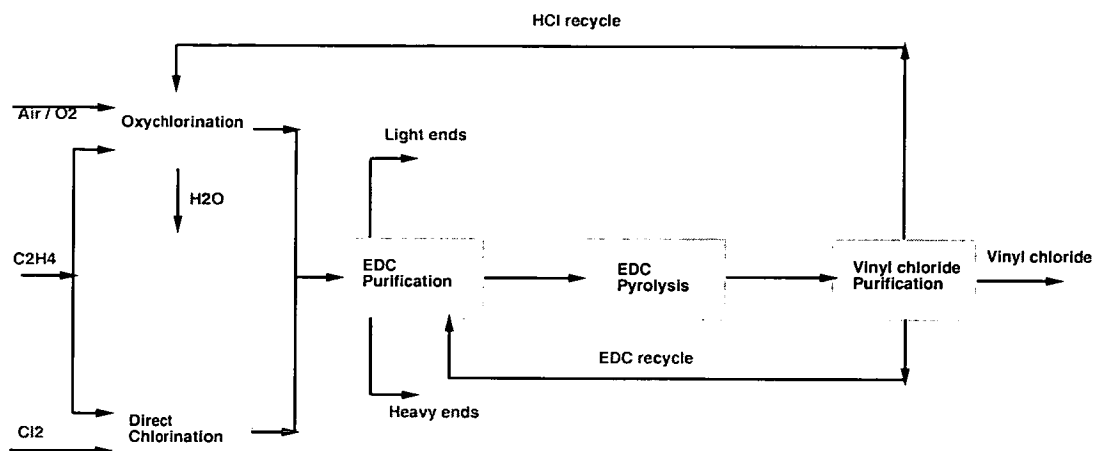
Figure 5.1: Vinyl chloride process block flowsheet

There are three main reactions involved :

- Direct chlorination
  $CH_2=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$

- Oxychlorination
  $CH_2=CH_2 + 2HCl + 1/2O_2 \rightarrow ClCH_2CH_2Cl + H_2O$

- EDC Pyrolysis
  $ClCH_2CH_2Cl \rightarrow CH_2=CHCl + HCl$

5.2.2   Process Description

Vinyl chloride monomer (VCM) is formed by direct chlorination and oxychlorination of ethylene followed by cracking of ethylene dichloride (EDC). During pyrolysis, EDC produces HCl as a byproduct which is recycled to the oxychlorinator. The oxychlorinator consumes HCl by reacting it with oxygen and ethylene, thus avoiding net production of HCl. The three reactors provide a balanced process between ethylene, chlorine and VCM.

The oxychlorinator involves a highly exothermic reaction and usually conducted at temperatures of 225-325 °C under pressures of 1-5 bar. The reaction temperature is carefully controlled at this level to avoid increasing the formation of byproducts, especially if the temperature goes above 325 °C. High temperatures would deactivate the catalyst as well as burn ethylene to carbon dioxide and carbon monoxide. The optimum operating condition gives 94-96 % EDC selectivity, 95-97 % HCl conversion and 94-97 % ethylene conversion. Byproducts normally obtained from the oxychlorinator are: vinyl chloride, ethyl chloride, 1,1-dichloroethane, vinylidene chloride, cis

and trans-1,2-dichloroethylenes, 1,1,2-trichloroethane, trichloroethylene, chloroform, carbon tetrachloride, methyl chloride, methylene chloride, chloral, chlorinated butanes, chlorinated aromatics and high boiling compounds.

Direct chlorination of ethylene produces 1,2-dichloroethane or ethylene dichloride (EDC) in liquid phase reactor with temperatures of 75-200 °C. EDC selectivity is very high, i.e. greater than 99 %. Industrially, the reaction is controlled by using $FeCl_3$ catalyst. Oxygen present as impurity in chlorine inhibits the formation of radicals leading to the generation of 1,1,2-trichloroethane. Conversion of ethylene is usually 100 %. Direct chlorination usually gives high purity of EDC suitable for cracking, except for the presence of ferric chloride ($FeCl_3$) which is the catalyst. $FeCl_3$ must be removed in advance to avoid rapid fouling in the cracking reactor.

The EDC that goes to pyrolysis must be very high purity and bone dry, normally more than 99.5 %. Trace amount of impurities that are carried along may lead to inhibition and fouling since chlorinated components are highly susceptible to cracking. In some processes, the bulk of the impurities can either be washed away with water and then caustic solution before the EDC stream is brought into purification, or they can also be removed by other means such as treatment with HCl, hydrogenation or adsorption on a solid.

Conventional cracking of EDC to vinyl chloride is conducted at temperatures of 425-550 °C and pressures of 14-30 bar. EDC conversion is about 50-60 % with selectivity of VCM ranging from 96-99 %. During cracking, other components are generated. These components act as inhibitors to the free radical sequence and lead to reduced EDC to VCM conversion. Among the byproducts found in the cracking reactor are: acetylene, ethylene, methyl chloride, butadiene, vinyl acetylene, benzene, chloropene, vinylidene chloride, 1,1-dichloroethane, chloroform, carbon tetrachloride and 1,1,1-trichloroethane. These species remain with EDC fraction and are recycled into the main process line.

5.2.3 Reaction analysis in chlorinators generated by the programs

The byproduct components found as a result of oxychlorination and direct chlorination reactions have been generated by the program. Most of the components have relatively high boiling points, so can be removed completely in the EDC purification section. However, some may be carried downstream and be recycled back into the reactor section. In this study, the condition of plausibility for species formation is set at 10 kJ/mol.

Reaction analysis in direct chlorinator

Electrophilic substitution facilitates the reaction between ethylene and chlorine. Polarized chlorine attacks double bond and replaces it with chlorine addition. Based on the substitution reaction mechanisms, the program generated a substantial amount of species, most of them are chlorinated. In the first level, the starting species consisted of ethylene and chlorine produced cyclobutane (C_4H_8), cyclobutene (C_4H_6),

cyclobutadiene (C_4H_4), $CH_2=CHCH_2CH_3$, $CH\equiv CH$, H_2, $ClCH_2CH_2Cl$, $ClCH=CH_2$. Reactions generated in **Level 1** are shown in the following list.

LEVEL 1

1. $2\ CH_2=CH_2 \rightarrow C_4H_8$
   $\Delta G_{298K} = -83.68$ (kJ/mol)

2. $2\ CH_2=CH_2 \rightarrow C_4H_4 + 2\ H_2$
   $\Delta G_{298K} = -23.76$ (kJ/mol)

3. $2\ CH_2=CH_2 \rightarrow CH_2=CHCH_2CH_3$
   $\Delta G_{298K} = -52.20$ (kJ/mol)

4. $2\ CH_2=CH_2 \rightarrow H_2 + C_4H_6$
   $\Delta G_{298K} = -53.72$ (kJ/mol)

5. $2\ CH_2=CH_2 \rightarrow H_2 + C_4H_6$
   $\Delta G_{298K} = -53.72$ (kJ/mol)

6. $CH_2=CH_2 + Cl_2 \rightarrow HCl + ClCH=CH_2$
   $\Delta G_{298K} = -114.88$ (kJ/mol)

7. $CH_2=CH_2 + Cl_2 \rightarrow HCl + CH\equiv CH$
   $\Delta G_{298K} = -42.78$ (kJ/mol)

8. $CH_2=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$
   $\Delta G_{298K} = -119.32$ (kJ/mol)

The next levels are the expansion of the surviving species. The expansion of nodes in **Level 2** are presented below.

LEVEL 2

1. Node 1 : $ClCH_2CH_2Cl$

   (a) $ClCH_2CH_2Cl \rightarrow HCl + CH_2=CHCl$
       $\Delta G_{298K} = 4.44$ (kJ/mol)
   (b) $2\ ClCH_2CH_2Cl \rightarrow ClCH_2CHCl_2 + ClCH_2CH_3$
       $\Delta G_{298K} = -2.44$ (kJ/mol)
   (c) $ClCH_2CH_2Cl \rightarrow CH_3CHCl_2$
       $\Delta G_{298K} = -2.44$ (kJ/mol)
   (d) $ClCH_2CH_2Cl + Cl_2 \rightarrow HCl + ClCH_2CHCl_2$
       $\Delta G_{298K} = -109.70$ (kJ/mol)

   There were 5 surviving species generated from Node 1 of Level 2 : $ClCH_2CHCl_2$, $ClCH_2CH_3$, $CH_2=CHCl$, HCl, CH_3CHCl_2.

2. Node 2 : $CH_2=CHCH_2CH_3$

(a) $CH_2=CHCH_2CH_3 \rightarrow CH_3CH=CHCH_3$
$\Delta G_{298K} = -7.62$ (kJ/mol)

(b) $CH_2=CHCH_2CH_3 + Cl_2 \nrightarrow HCl + CH_2=[Cl]CCH_2CH_3$
$\Delta G_{298K} = -115.81$ (kJ/mol)

(c) $CH_2=CHCH_2CH_3 + Cl_2 \rightarrow HCl + ClCH=CHCH_2CH_3$
$\Delta G_{298K} = -114.88$ (kJ/mol)

(d) $CH_2=CHCH_2CH_3 + Cl_2 \rightarrow 2\ HCl + CH\equiv CHCH_2CH_3$
$\Delta G_{298K} = -55.43$ (kJ/mol)

3. Node 3 : $ClCH=CH_2$

(a) $2\ ClCH=CH_2 \rightarrow HCl + ClCH=CHCH=CH_2$
$\Delta G_{298K} = -40.14$ (kJ/mol)

(b) $2\ ClCH=CH_2 \rightarrow Cl_2C=CH_2 + CH_2=CH_2$
$\Delta G_{298K} = -0.93$ (kJ/mol)

(c) $ClCH=CH_2 + Cl_2 \rightarrow HCl + ClCH=CHCl$
$\Delta G_{298K} = -114.88$ (kJ/mol)

(d) $ClCH=CH_2 + Cl_2 \rightarrow HCl + Cl_2C=CH_2$
$\Delta G_{298K} = -115.81$ (kJ/mol)

(e) $ClCH=CH_2 + Cl_2 \rightarrow HCl + ClC\equiv CH$
$\Delta G_{298K} = -55.43$ (kJ/mol)

The surviving species show that further chlorine substitution prevails during the course of the reaction. Beside that, the program also generates species having double bond and cyclic chain. The species tree can be seen in Figure 5.2.
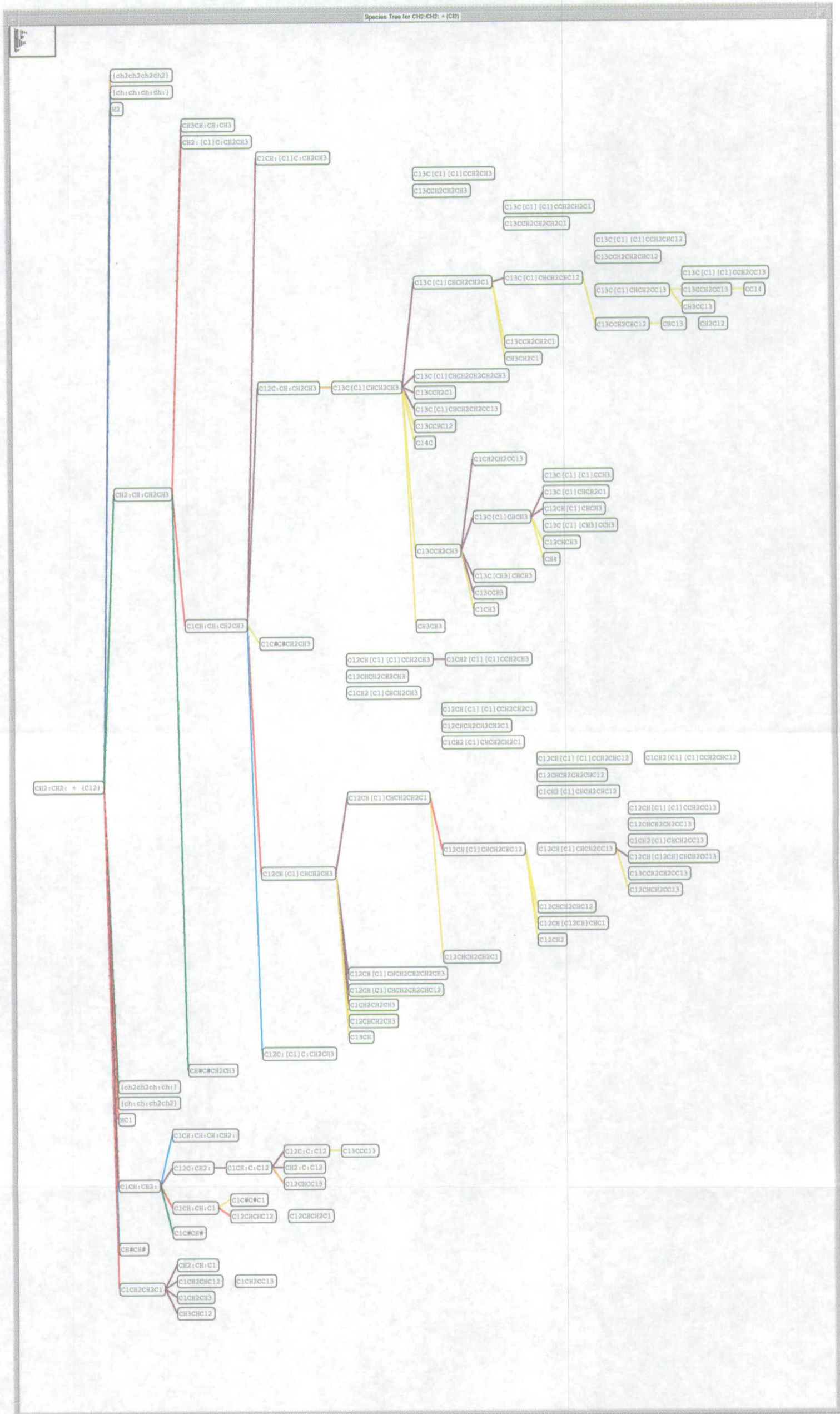
Figure 5.2: Species tree of direct chlorination

Reaction analysis in oxychlorinator

Beside electrophilic substitution, oxidation reactions occur in the oxychlorinator due to the presence of oxygen. New species generation involves addition reaction of chlorine, oxidation reaction and HCl decomposition. The starting species consisted of the following components : $CH_2=CH_2$, HCl, Cl_2, O_2, H_2O. The first level generates compounds such as : HCl, $ClCH=CH_2$, $CH_2=CHCH_2CH_3$, CH_2O, $OHCH_2CH_3$, $ClCH_2CH_2Cl$, $OHCH=CHOH$ and $ClCH_2CH_3$. Reactions involved in generating these species are :

LEVEL 1

1. $2\ CH_2=CH_2 \rightarrow CH_2=CHCH_2CH_3$
   $\Delta G_{298K} = -52.20\ (kJ/mol)$

2. $CH_2=CH_2 + O_2 \rightarrow 2\ CH_2O$
   $\Delta G_{298K} = -281.42\ (kJ/mol)$

3. $CH_2=CH_2 + O_2 \rightarrow OHCH=CHOH$
   $\Delta G_{298K} = -288.88\ (kJ/mol)$

4. $CH_2=CH_2 + HCl \rightarrow ClCH_2CH_3$
   $\Delta G_{298K} = -12.06\ (kJ/mol)$

5. $CH_2=CH_2 + Cl_2 \rightarrow HCl + ClCH=CH_2$
   $\Delta G_{298K} = -114.88\ (kJ/mol)$

6. $CH_2=CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$
   $\Delta G_{298K} = -119.32\ (kJ/mol)$

7. $CH_2=CH_2 + H_2O \rightarrow OHCH_2CH_3$
   $\Delta G_{298K} = -3.48\ (kJ/mol)$

It can be seen that oxidation of ethylene occurs beside chlorine addition and substitution reactions. The next level comprises further oxidation and substitution reactions.

LEVEL 2

1. Node 1 : the reaction of $ClCH_2CH_2Cl$

   (a) $ClCH_2CH_2Cl \rightarrow HCl + CH_2=CHCl$
       $\Delta G_{298K} = 4.44\ (kJ/mol)$

   (b) $2\ ClCH_2CH_2Cl \rightarrow ClCH_2CHCl_2 + ClCH_2CH_3$
       $\Delta G_{298K} = -2.44\ (kJ/mol)$

   (c) $ClCH_2CH_2Cl + Cl_2 \rightarrow HCl + ClCH_2CHCl_2$
       $\Delta G_{298K} = -109.70\ (kJ/mol)$

2. Node 2 : the reaction of $CH_2=CHCH_2CH_3$

(a) $CH_2=CHCH_2CH_3 \rightarrow CH_3CH=CHCH_3$
$\Delta G_{298K} = -7.62$ (kJ/mol)

(b) $CH_2=CHCH_2CH_3 + O_2 \rightarrow H_2O + CH_2=CHCOCH_3$
$\Delta G_{298K} = -357.72$ (kJ/mol)

(c) $CH_2=CHCH_2CH_3 + O_2 \rightarrow CHOCH_2CH_3 + CH_2O$
$\Delta G_{298K} = -305.78$ (kJ/mol)

(d) $CH_2=CHCH_2CH_3 + O_2 \rightarrow CH_2=CH[OH][OH]CCH_3$
$\Delta G_{298K} = -270.80$ (kJ/mol)

(e) $CH_2=CHCH_2CH_3 + O_2 \rightarrow OHCH=[OH]CCH_2CH_3$
$\Delta G_{298K} = -281.81$ (kJ/mol)

(f) $CH_2=CHCH_2CH_3 + HCl \rightarrow ClCH_2CH_2CH_2CH_3$
$\Delta G_{298K} = -4.44$ (kJ/mol)

(g) $CH_2=CHCH_2CH_3 + HCl \rightarrow CH_3CH_2[Cl]CHCH_3$
$\Delta G_{298K} = -6.88$ (kJ/mol)

(h) $CH_2=CHCH_2CH_3 + H_2O \rightarrow OHCH_2CH_2CH_2CH_3$
$\Delta G_{298K} = 4.14$ (kJ/mol)

(i) $CH_2=CHCH_2CH_3 + H_2O \rightarrow CH_3[OH]CH_2CH_2CH_3$
$\Delta G_{298K} = 1.70$ (kJ/mol)

(j) $CH_2=CHCH_2CH_3 + H_2O \rightarrow CH_3CH_2[OH]CHCH_3$
$\Delta G_{298K} = 1.70$ (kJ/mol)

3. Node 3 : $OHCH=CHOH$

(a) $OHCH=CHOH + O2 \rightarrow 2\ HCOOH$
$\Delta G_{298K} = -474.94$ (kJ/mol)

4. Node 4 : $ClCH=CH_2$

(a) $2\ ClCH=CH_2 \rightarrow HCl + ClCH=CHCH=CH_2$
$\Delta G_{298K} = -40.14$ (kJ/mol)

(b) $2\ ClCH=CH_2 \rightarrow Cl_2C=CH_2 + CH_2=CH_2$
$\Delta G_{298K} = -0.93$ (kJ/mol)

(c) $ClCH=CH_2 + HCl \rightarrow ClCH_2CH_2Cl$
$\Delta G_{298K} = -4.44$ (kJ/mol)

(d) $ClCH=CH_2 + HCl \rightarrow Cl_2CHCH_3$
$\Delta G_{298K} = -6.88$ (kJ/mol)

(e) $ClCH=CH_2 + Cl_2 \rightarrow HCl + ClCH=CHCl$
$\Delta G_{298K} = -114.88$ (kJ/mol)

(f) $ClCH=CH_2 + Cl_2 \rightarrow HCl + Cl_2C=CH_2$
$\Delta G_{298K} = -115.81$ (kJ/mol)

(g) $ClCH=CH_2 + H_2O \rightarrow HCl + OHCH=CH_2$
$\Delta G_{298K} = 8.58$ (kJ/mol)

5. Node 5 : CH_2O

(a) $2\,CH_2O \rightarrow CO_2 + CH_4$
$\Delta G_{298K} = -225.47$ (kJ/mol)

(b) $CH_2O \rightarrow CO + H_2$
$\Delta G_{298K} = -27.40$ (kJ/mol)

(c) $CH_2O + O_2 \rightarrow CO_2 + H_2O$
$\Delta G_{298K} = -513.40$ (kJ/mol)

(d) $CH_2O + Cl_2 \rightarrow CO + 2\,HCl$
$\Delta G_{298K} = -218.06$ (kJ/mol)

(e) $CH_2O + H_2O \rightarrow CO_2 + 2\,H_2$
$\Delta G_{298K} = -55.80$ (kJ/mol)

The above results show that a number of chlorinated and oxygenated species may be generated in the oxychlorinator. Water is also produced. The species tree diagram is shown in Figure 5.3.
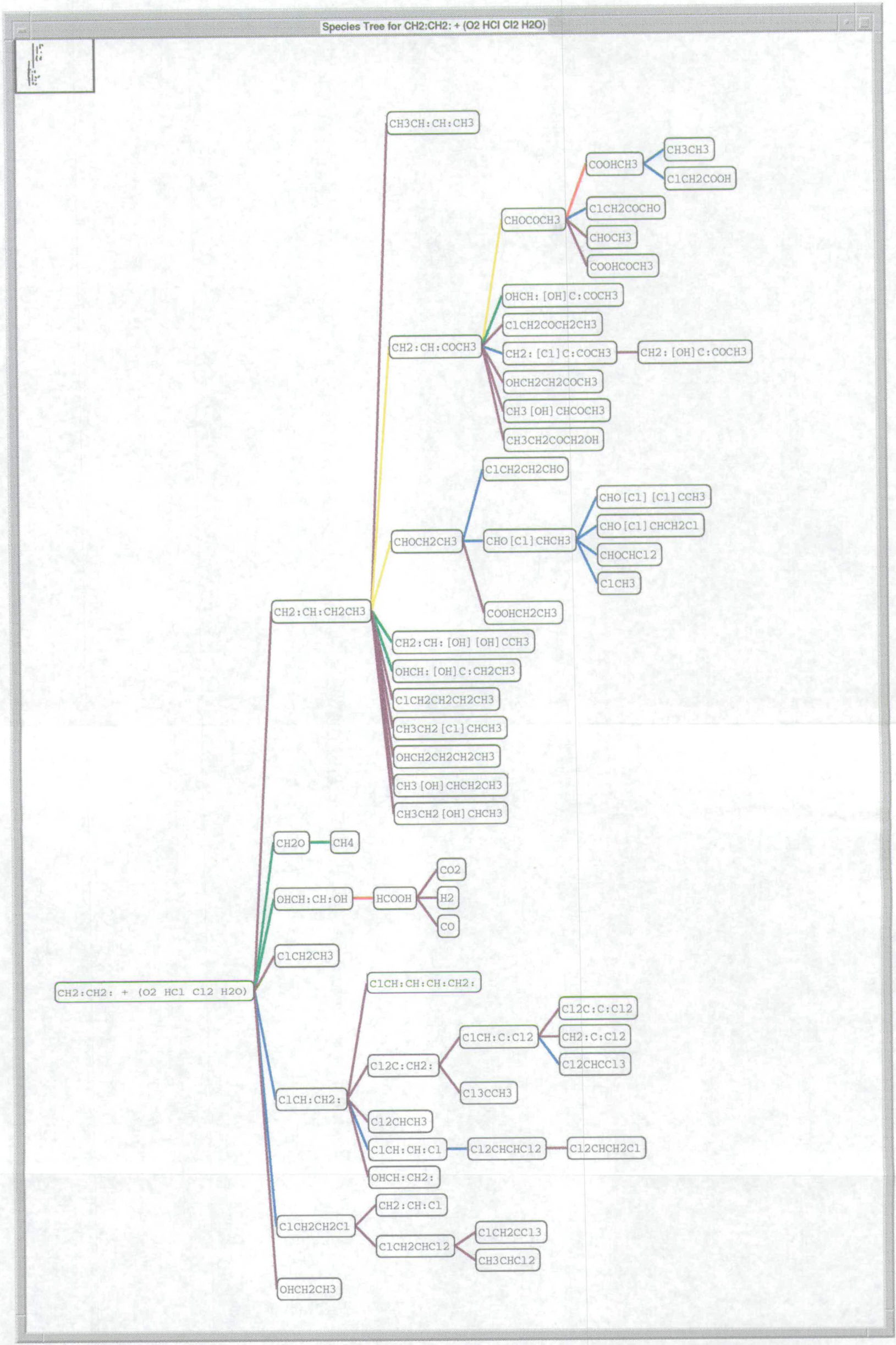
Figure 5.3: Species tree of oxychlorination

5.2.4 List of byproducts having close boiling points

Chlorinated compounds have relatively high boiling points, likewise those of oxygenated compounds. These components may undergo sharp separation and are completely removed from EDC stream. Some of the compounds however have boiling points close to EDC. These components may create problem as sharp separation is almost unlikely. The following is the list of byproducts having close boiling point relative to the key component, i.e. EDC (ethylene dichloride).

Table 5.1: Component boiling points

Component	Boiling point, C
HCl	-85
$CH_3CH_2[Cl]CHCH_3$	68.2
$CH_2=CHCH=CHCH_2CH_3$	73
$Cl[CH_3]CCl_2$	74.1
CCl_4	76.5
$ClCH_2CH_2CH_2CH_3$	78.4
CH_3CH_2OH	78.5
C_6H_6	80.1
$CH_3[OH]CHCH_3$	82.4
$ClCH_2CH_2Cl$ (EDC)	**83.5**
$ClCH_2CHO$	85.5
$ClCHCCl_2$	87
Cl_2CHCHO	90.0
$CH_2=[Cl]CCH_2Cl$	94
$CH_3[ClCH_2]CHCl$	96.4
$OHCH_2CH_2CH_3$	97.4
Cl_3CCHO	97.9
$CH_3CH_2[OH]CHCH_3$	99.5
H_2O	100

5.2.5 EDC Purification

The products of both reactors flow into EDC purification section where byproducts have to be removed before entering pyrolysis section. EDC entering pyrolysis must have high purity which is typically greater than 99.5 % and contain less than 10 ppm water. In the purification section, EDC is removed in two columns, the first column is used to separate 'light' components while the second column is used to remove the 'heavy' components. Procedures for the separation simulation are set out below.

1. K-values and Relative Volatility
   The component K-values are determined by carrying a phase equilibrium calculation using ASPEN with 50 % vapour fraction and pressure at 1 atm corresponding to 82.6 °C. The mole flowrate of EDC was set at 20 kmol/hr while other components were set to a nominally small amount of 0.1 kmol/hr. The relatively

very small amount of byproducts is considered here due to unknown kinetics of side reactions. It is also assumed that the main reactions have high conversion, therefore it is unlikely for the byproducts to be produced in significant amount. The relative volatility of components was calculated using the ratio of K-values relative to the key component. The results can be seen in Table 5.2. The order of the component boiling points does not correspond with the order of the relative volatility which is an indication of nonideal mixture. Therefore, the formation of azeotrope is likely.

2. RADFRAC Simulation

RADFRAC model is a rigorous fractionation model used in ASPEN Simulation Package. The purpose is to run rigorous rating and design calculations for single ordinary distillation column, azeotropic column, reactive or extractive distillation column. In this study, we use it as an ordinary distillation column. Ethylene dichloride purification takes place in two columns. Two flowsheets were considered to hold direct and indirect separation sequences. In direct separation, the first column takes EDC overhead. The overheads of the first column go to the second column where purified EDC is removed in the bottom section. As for indirect separation, EDC in the first column goes to the bottom and is then removed as overheads in the second column.

Direct Separation Sequence

The configuration of direct separation simulation using ASPEN is shown in figure 5.4. Column-1 features the separation of key component EDC as the light key and $ClCH_2CHO$ as the heavy key. Partial condensation is used in the overhead cooling where a stream containing most volatile component such as HCl remains in vapour phase. Otherwise, steady state condition could not be achieved. An EDC-rich stream is taken in the outlet retaining its liquid phase. The HCl and EDC-rich streams are fed to Column-2 where EDC is separated as the heavy key component and taken in the bottom product.

The component boiling points and relative volatility as calculated and mentioned before are presented in Table 5.2. Both separation columns have 50 stages and reflux ratio of 5.0. The results are shown in Table 5.3 where the component flows in each stream are depicted. The percentage of EDC in the product stream is found to be 95.36 %, and the recovery of EDC in the first column is 98.65 %.
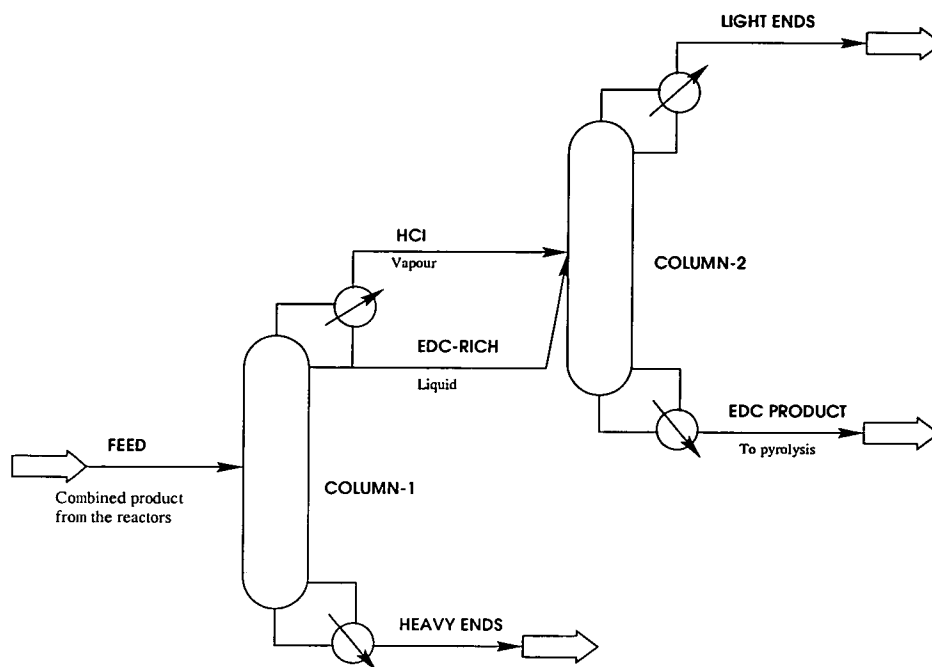
Figure 5.4: EDC Purification Simulation : Direct Sequence

Table 5.2: Component Boiling Points and Relative Volatility

Component	Boiling point, $^\circ$C	Relative Volatility
HCl	-85	112.1556
CH_3CH_2OH	78.5	5.962124
H_2O	100	4.373645
$CH_3[OH]CHCH_3$	82.4	2.426414
CCl_4	76.5	1.931471
$CH_2{=}CHCH{=}CHCH_2CH_3$	73	1.588170
$ClCH_2CH_2CH_2CH_3$	78.4	1.503247
$CH_3CH_2[Cl]CHCH_3$	68.2	1.490158
$CH_3CH_2[OH]CHCH_3$	99.5	1.377806
$ClCHCCl_2$	87	1.279475
C_6H_6	80.1	1.188883
$\mathbf{ClCH_2CH_2Cl}$ **(EDC)**	**83.5**	**1.000000**
$ClCH_2CHO$	85.5	0.9220876
Cl_3CCHO	97.9	0.8230973
Cl_2CHCHO	90.0	0.8228010
$CH_2{=}[Cl]CCH_2Cl$	94	0.7069781
$OHCH_2CH_2CH_3$	97.4	0.6575679
$CH_3[ClCH_2]CHCl$	96.4	0.6565234
$Cl[CH_3]CCl_2$	74.1	0.3667172

Table 5.3: Separability of components in direct separation, component flow in kmol/hr

Streams	FEED	HCL	EDC-RICH	HEAVY ENDS	EDC PRODUCT	LIGHT ENDS
From Units		COLUMN-1	COLUMN-1	COLUMN-1	COLUMN-2	COLUMN-2
To Units	COLUMN-1	COLUMN-2	COLUMN-2			
Phase	LIQUID	VAPOR	LIQUID	LIQUID	LIQUID	VAPOUR
Temperature [C]	20.0	80.2	80.2	89.9	81.8	73.3
Pressure [BAR]	1.0	1.0	1.0	1.0	1.0	1.0
Mole flow [KMOL/HR]	21.8	2.1	18.9	0.8	20.3	0.7
Components						
HCl	0.1	0.092	0.008	trace	trace	0.1
CH_3CH_2OH	0.1	0.039	0.061	trace	0.028	0.072
H_2O	0.1	0.031	0.069	trace	0.048	0.052
$CH_3[OH]CHCH_3$	0.1	0.020	0.080	trace	0.072	0.028
CCl_4	0.1	0.017	0.083	trace	0.081	0.019
$CH_2{=}CHCH{=}CHCH_2CH_3$	0.1	0.014	0.086	trace	0.088	0.012
$ClCH_2CH_2CH_2CH_3$	0.1	0.013	0.087	trace	0.089	0.011
$CH_3CH_2[Cl]CHCH_3$	0.1	0.013	0.087	trace	0.089	0.011
$CH_3CH_2[OH]CHCH_3$	0.1	0.012	0.088	< 0.001	0.091	0.009
$ClCHCCl_2$	0.1	0.012	0.088	trace	0.093	0.007
C_6H_6	0.1	0.011	0.089	trace	0.095	0.005
$ClCH_2CH_2Cl$ (EDC)	**20.0**	**1.813**	**17.917**	**0.270**	**19.358**	**0.371**
$ClCH_2CHO$	0.1	0.008	0.089	0.003	0.096	< 0.001
Cl_3CCHO	0.1	0.002	0.025	0.073	0.027	trace
Cl_2CHCHO	0.1	0.003	0.042	0.054	0.046	< 0.001
$CH_2{=}[Cl]CCH_2Cl$	0.1	< 0.001	0.001	0.099	0.001	trace
$OHCH_2CH_2CH_3$	0.1	< 0.001	0.001	0.1	< 0.001	trace
$CH_3[ClCH_2]CHCl$	0.1	trace	< 0.001	0.1	< 0.001	trace
$Cl[CH_3]CCl_2$	0.1	trace	trace	0.1	trace	trace

Indirect Separation Sequence
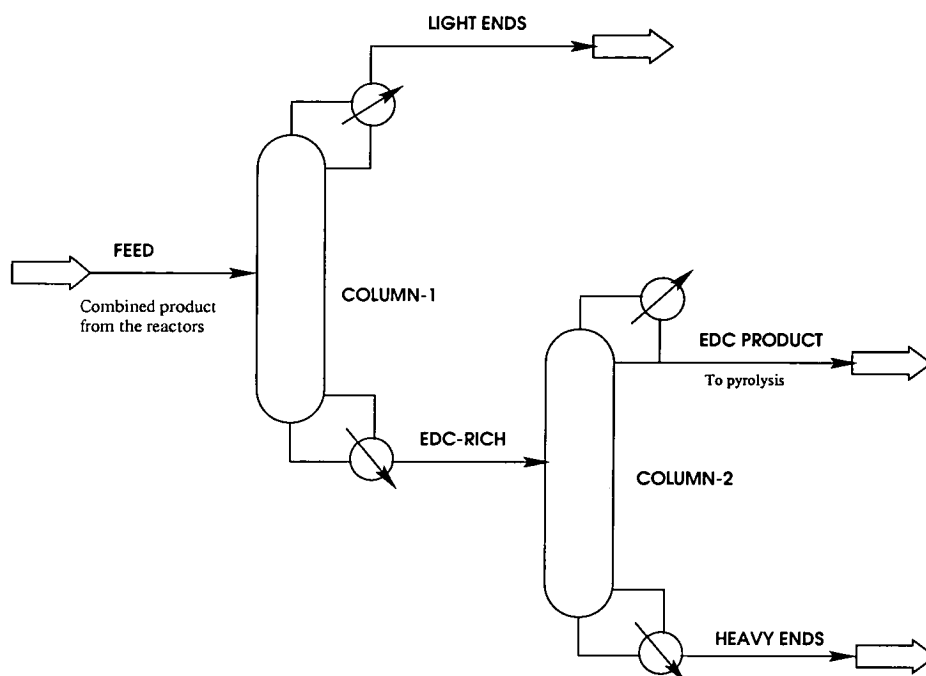
Figure 5.5: EDC Purification Simulation : Indirect Sequence

For indirect sequence, the light key component is C_6H_6 while the heavy key component is EDC. The component relative volatilities are similar to that in Table 5.2.

The results of the indirect sequence separation are presented in the following table with reflux ratio of 5.0 and the number of stages 50. The percentage of EDC in the product stream equals 96.15 %, and the recovery in the first column is 97.04 %.

Table 5.4: Separability of components in indirect separation, component flow in kmol/hr

Streams	FEED	LIGHT ENDS	EDC-RICH	EDC PRODUCT	HEAVY ENDS
From Units		COLUMN-1	COLUMN-1	COLUMN-2	COLUMN-2
To Units	COLUMN-1		COLUMN-2		
Phase	LIQUID	VAPOR	LIQUID	LIQUID	LIQUID
Temperature [C]	20.0	72.4	83.1	82.8	90.2
Pressure [BAR]	1.0	1.0	1.0	1.0	1.0
Mole flow [KMOL/HR]	21.8	1.1	20.7	19.9	0.8
Components					
HCl	0.1	0.1	trace	0.0	0.0
CH_3CH_2OH	0.1	0.1	trace	trace	trace
H_2O	0.1	0.1	trace	trace	trace
$CH_3[OH]CHCH_3$	0.1	0.069	0.031	0.031	trace
CCl_4	0.1	0.040	0.060	0.060	trace
$CH_2=CHCH=CHCH_2CH_3$	0.1	0.022	0.078	0.078	trace
$ClCH_2CH_2CH_2CH_3$	0.1	0.019	0.081	0.081	trace
$CH_3CH_2[Cl]CHCH_3$	0.1	0.020	0.080	0.080	trace
$CH_3CH_2[OH]CHCH_3$	0.1	0.015	0.085	0.085	< 0.001
$ClCHCCl_2$	0.1	0.012	0.088	0.088	trace
C_6H_6	0.1	0.009	0.091	0.091	trace
$ClCH_2CH_2Cl$ (EDC)	20.0	0.593	19.407	19.133	0.274
$ClCH_2CHO$	0.1	0.001	0.099	0.096	0.003
Cl_3CCHO	0.1	< 0.001	0.1	0.030	0.070
Cl_2CHCHO	0.1	< 0.001	0.1	0.046	0.054
$CH_2=[Cl]CCH_2Cl$	0.1	trace	0.1	0.001	0.099
$OHCH_2CH_2CH_3$	0.1	trace	0.1	< 0.001	0.1
$CH_3[ClCH_2]CHCl$	0.1	trace	0.1	< 0.001	0.1
$Cl[CH_3]CCl_2$	0.1	trace	0.1	trace	0.1

Summary of EDC Purification

The direct separation shows that EDC taken as the bottom product in column-2 carries most of the 'light' components. This is indicated by larger fraction of 'light' components in the bottom product than that in the top product. Most of these components have close boiling points relative to EDC, while HCl which has much lower boiling point can be all separated and taken entirely in the light stream. Therefore, the overhead stream would contain mostly HCl with smaller fraction of the 'light' components. Similar occurence is found in the indirect separation. In column-1 where EDC is taken as the bottom product, most of the 'light' components are carried with EDC to the second column. In the second column, where EDC is taken overhead, it carries all 'light' components which have been brought along from the first column. In addition to that, there is also a significant amount of heavy components. It can be seen that, the fraction of heavy key component $ClCH_2CHO$ carried over to the top is much larger than its fraction remaining in the bottom. It is apparent that sharp separation is not possible. The following table (Table 5.5) shows the comparison of composition of the EDC stream between direct and indirect sequences in both columns.

The table illustrates EDC recovery in the first column of a direct separation which is higher than that of an indirect separation. Likewise, the recovery of the EDC in the second column of a direct separation is also higher than that of an indirect separation. However, the product purity in the indirect sequence is better than that of the direct sequence. This is because the direct sequence evidently carries more 'light' components than the indirect sequence while at the same time the amount of 'heavy' components taken overhead is fairly large.

In respect of the indirect sequence, most 'light' components are separated in the first column, so less amount of these components are brought into the second column. Consequently, the purity of EDC in the product stream is higher that of the direct sequence. In terms of EDC recovery, the results are in consistence with the common belief which suggests the use of the direct sequence for high recovery. However, the use of indirect sequence is better in providing high purity for the separation of a fairly light product, which is in contrast to the usual practice.

The components which cannot be separated from EDC during purification, would be carried along into the pyrolysis section. Further reactions, mostly chlorinated since pyrolysis is induced with CCl_4, occur. The following section discusses the possibility of reactions found in the pyrolysis section.

Table 5.5: Comparison of composition in the EDC stream, component flow in kmol/hr

Components	Indirect sequence First column	Direct sequence First column	Indirect sequence Second column	Direct sequence Second column
HCl	trace	0.1	0.0	trace
CH_3CH_2OH	trace	0.1	trace	0.028
H_2O	trace	0.1	trace	0.048
$CH_3[OH]CHCH_3$	0.031	0.1	0.031	0.072
CCl_4	0.060	0.1	0.060	0.081
$CH_2=CHCH=CHCH_2CH_3$	0.078	0.1	0.078	0.088
$ClCH_2CH_2CH_2CH_3$	0.081	0.1	0.081	0.089
$CH_3CH_2[Cl]CHCH_3$	0.080	0.1	0.080	0.089
$CH_3CH_2[OH]CHCH_3$	0.085	0.1	0.085	0.091
$ClCHCCl_2$	0.088	0.1	0.088	0.093
C_6H_6	0.091	0.1	0.091	0.095
$ClCH_2CH_2Cl$ (EDC)	19.407	19.73	19.133	19.358
$ClCH_2CHO$	0.099	0.097	0.096	0.096
Cl_3CCHO	0.1	0.027	0.030	0.027
Cl_2CHCHO	0.1	0.045	0.046	0.046
$CH_2=[Cl]CCH_2Cl$	0.1	0.001	0.001	0.001
$OHCH_2CH_2CH_3$	0.1	0.001	< 0.001	< 0.001
$CH_3[ClCH_2]CHCl$	0.1	< 0.001	< 0.001	< 0.001
$Cl[CH_3]CCl_2$	0.1	trace	trace	trace
Total	20.7	21	19.9	20.3
Percent recovery	97.04	98.65	95.67	96.79

5.2.6 Reaction Analysis at the Pyrolysis Section

Assuming that some oxidized and chlorinated compounds might inevitably enter the pyrolysis section where further chlorination occurs. In order to initiate the chain reaction, CCl_4 is injected into the pyrolysis reactor. The compounds carried over from the previous reactors and the separation section will react with CCl_4 and form new species.

Pyrolytic decomposition causes C-C and C-H bond fissions forming lower chains and dehydrogenation. As a result, most species are heavily chlorinated and some will generate double bonds. Oxidized groups will be cleaved and decomposed. Species formation and the species tree are presented in the following section. The results are divided into two parts; the first part consists of the main reaction of EDC and CCl4 to demonstrate the formation of chlorinated components, while the second part includes the reactions of some oxygenated compounds.

Reaction of Pure EDC and CCl_4

Starting species : $ClCH_2CH_2Cl$, CCl_4
LEVEL 1

Feasible reactions generated from the initial species are as follows :

1. $ClCH_2CH_2Cl \rightarrow HCl + CH_2{=}CHCl$
   $\Delta G_{298K} = 4.44$ (kJ/mol)

2. $2\ ClCH_2CH_2Cl \rightarrow ClCH_2CHCl_2 + ClCH_2CH_3$
   $\Delta G_{298K} = -2.44$ (kJ/mol)

3. $ClCH_2CH_2Cl \rightarrow CH_3CHCl_2$
   $\Delta G_{298K} = -2.44$ (kJ/mol)

4. $ClCH_2CH_2Cl \rightarrow CHCl_3 + ClCH_2CHCl_2$
   $\Delta G_{298K} = -7.72$ (kJ/mol)

There are 6 surviving species generated from the above reactions: HCl, $CH_2{=}CHCl$, $ClCH_2CHCl_2$, $ClCH_2CH_3$, CH_3CHCl_2 and $CHCl_3$. The expansion of the surviving species resulted from **Level 1** can be seen in **Level 2** as follows :
LEVEL 2

1. Node 1 : reaction of CH_3CHCl_2

   (a) $2\ CH_3CHCl_2 \rightarrow ClCH_2CHCl_2 + CH_3CH_2Cl$
      $\Delta G_{298K} = 2.44$ (kJ/mol)

   (b) $2\ CH_3CHCl_2 \rightarrow CH_3CCl_3 + CH_3CH_2Cl$
      $\Delta G_{298K} = 7.72$ (kJ/mol)

   (c) $2\ CH_3CHCl_2 \rightarrow Cl_2CHCH_2CHCl_2 + CH_4$
      $\Delta G_{298K} = -8.41$ (kJ/mol)

(d) $2\ CH_3CHCl_2 \rightarrow CH_3CH_2CHCl_2 + CH_2Cl_2$
$\Delta G_{298K} = 2.44\ (kJ/mol)$

(e) $2\ CH_3CHCl_2 \rightarrow CH_3[CH_3]CCl_2 + CH_2Cl_2$
$\Delta G_{298K} = 7.72\ (kJ/mol)$

(f) $CH_3CHCl_2 + CCl_4 \rightarrow HCl + Cl_3CCH_2CHCl_2$
$\Delta G_{298K} = -32.52\ (kJ/mol)$

(g) $CH_3CHCl_2 + CCl_4 \rightarrow ClCH_2CHCl_2 + CHCl_3$
$\Delta G_{298K} = -5.28\ (kJ/mol)$

(h) $CH_3CHCl_2 + CCl_4 \rightarrow Cl_2CHCHCl_2 + CH_2Cl_2$
$\Delta G_{298K} = -5.28\ (kJ/mol)$

(i) $CH_3CHCl_2 + CCl_4 \rightarrow CH_4 + Cl_3CCCl_3$
$\Delta G_{298K} = -3.13\ (kJ/mol)$

2. Node 2 : reaction of $ClCH_2CH_3$

(a) $ClCH_2CH_3 \rightarrow CH_2{=}CH_2 + HCl$
$\Delta G_{298K} = -3.46\ (kJ/mol)$

(b) $2\ ClCH_2CH_3 \rightarrow C_4H_8 + 2\ HCl$
$\Delta G_{298K} = -59.56\ (kJ/mol)$

(c) $2\ ClCH_2CH_3 \rightarrow HCl + ClCH_2CH_2CH_2CH_3$
$\Delta G_{298K} = -32.52\ (kJ/mol)$

(d) $2\ ClCH_2CH_3 \rightarrow Cl_2CHCH_3 + CH_3CH_3$
$\Delta G_{298K} = -2.44\ (kJ/mol)$

(e) $ClCH_2CH_3 + CCl_4 \rightarrow ClCH_2CH_2CCl_3 + HCl$
$\Delta G_{298K} = -32.52\ (kJ/mol)$

(f) $ClCH_2CH_3 + CCl_4 \rightarrow CHCl_3 + ClCH_2CH_2Cl$
$\Delta G_{298K} = -5.28\ (kJ/mol)$

(g) $ClCH_2CH_3 + CCl_4 \rightarrow CHCl_3 + Cl_2CHCH_3$
$\Delta G_{298K} = -7.72\ (kJ/mol)$

Some of the new species formed in the pyrolysis section are shown in Table 5.2.6. The following figure (Fig 5.6) shows the species tree of species formation in the pyrolysis section.
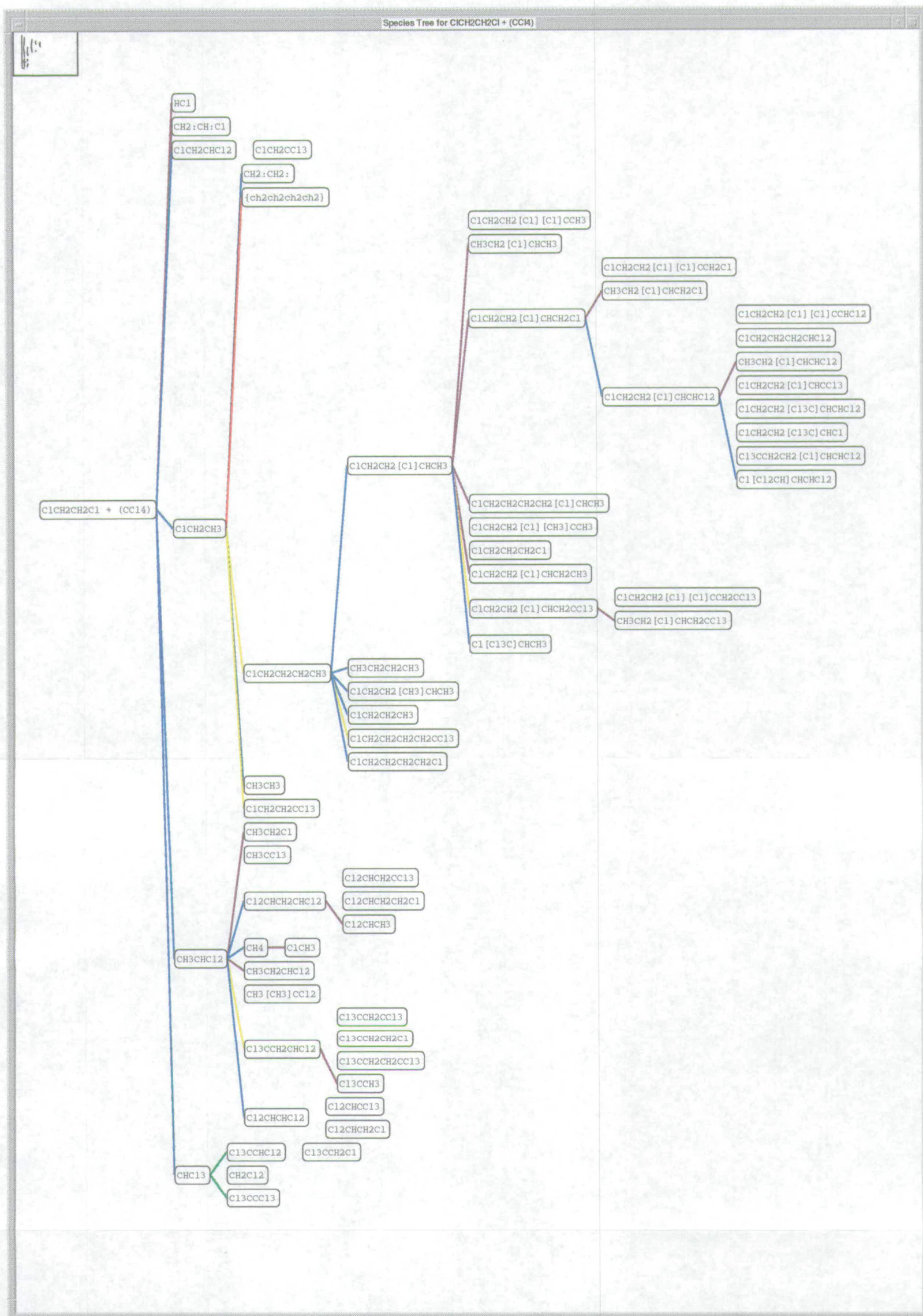
Figure 5.6: Species tree of pyrolysis reactions of pure EDC

Pyrolysis Reaction of Some Oxygenated Components

This section demonstrates the fate of oxygenated compounds in the pyrolysis reactor. Propanol and chloroacetaldehyde were taken as examples and run in two batches. The species trees are illustrated in Figure 5.7.

Starting species : CH_3CH_2CHO, CCl_4, H_2O
LEVEL 1

1. $CH_3CH_2CHO + H_2O \rightarrow H_2 + CO_2 + CH_3CH_3$
   $\Delta G_{298K} = -74.70$ (kJ/mol)

2. $CH_3CH_2CHO + H_2O \rightarrow H_2 + CH_3CH_2COOH$
   $\Delta G_{298K} = -15.59$ (kJ/mol)

3. $CH_3CH_2CHO + CCl_4 + H_2O \rightarrow HCl + CHCl_3 + CH_3CH_2COOH$
   $\Delta G_{298K} = -104.27$ (kJ/mol)

The aldehyde group will be decomposed into carbon dioxide or transformed into carboxylate. The surviving species emerged from this level consist of those which have been devoid of carbonyl groups or transformed into more stable material such as acid. The following reactions show how carboxylate decomposed and no new carbonyl groups were formed. If alcohol is formed, it will lead to the formation of aldehyde and thus will be destroyed.

LEVEL 2

1. Node 1: Transformation of CH_3CH_2COOH

   (a) $CH_3CH_2COOH \rightarrow CH_3CH_3 + CO_2$
       $\Delta G_{298K} = -59.11$ (kJ/mol)

   (b) $2\ CH_3CH_2COOH \rightarrow H2 + 2CO2 + CH3CH2CH2CH3$
       $\Delta G_{298K} = -67.34$ (kJ/mol)

   (c) $CH_3CH_2COOH + CCl_4 \rightarrow ClCH_2CH_3 + CO_2 + CHCl_3$
       $\Delta G_{298K} = -64.39$ (kJ/mol)

   (d) $CH_3CH_2COOH + CCl_4 \rightarrow CH_3CH_2CCl_3 + CO_2 + HCl$
       $\Delta G_{298K} = -91.63$ (kJ/mol)

2. Node 2: Transformation of $CHCl_3$

   (a) $2\ CHCl_3 \rightarrow HCl + Cl_3CCHCl_2$
       $\Delta G_{298K} = -27.24$ (kJ/mol)

   (b) $2\ CHCl_3 \rightarrow CCl_4 + CH_2Cl_2$
       $\Delta G_{298K} = -7.72$ (kJ/mol)

   (c) $CHCl_3 + CCl_4 \rightarrow HCl + Cl_3CCCl_3$
       $\Delta G_{298K} = -27.24$ (kJ/mol)

Starting species : $ClCH_2CHO$, CCl_4, H_2O
LEVEL 1

1. $ClCH_2CHO + H_2O \rightarrow H_2 + CO_2 + ClCH_3$
$\Delta G_{298K} = -74.70$ (kJ/mol)

2. $ClCH_2CHO + CCl_4 + H_2O \rightarrow HCl + CO_2 + 2\ Cl_2CH_2$
$\Delta G_{298K} = -160.94$ (kJ/mol)

LEVEL 2

1. Node 1: reaction of Cl_2CH_2

   (a) $Cl_2CH_2 + CCl_4 \rightarrow HCl + Cl_2CHCCl_3$
   $\Delta G_{298K} = -34.96$ (kJ/mol)

   (b) $Cl_2CH_2 + CCl_4 \rightarrow 2\ CHCl_3$
   $\Delta G_{298K} = -7.72$ (kJ/mol)

2. Node 2: The reaction of $ClCH_3$

   (a) $ClCH_3 + CCl_4 \rightarrow HCl + ClCH_2CCl_3$
   $\Delta G_{298K} = -32.52$ (kJ/mol)

   (b) $ClCH_3 + CCl_4 \rightarrow CHCl_3 + Cl_2CH_2$
   $\Delta G_{298K} = -5.28$ (kJ/mol)

Figure 5.7 shows the tree diagram of the pyrolysis reaction of the oxygenated compounds. The species generated are mostly chlorinated, while other types of species are not generated.
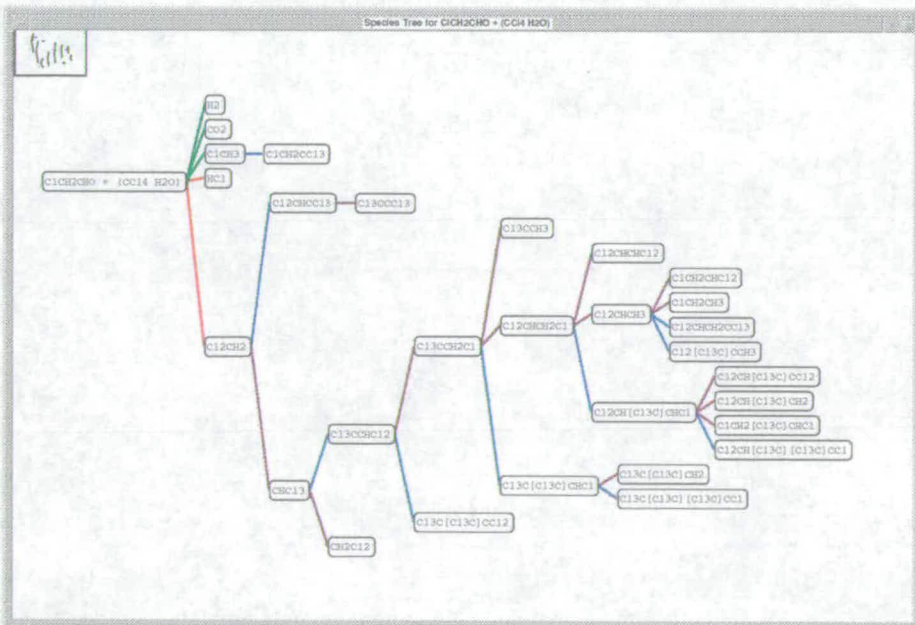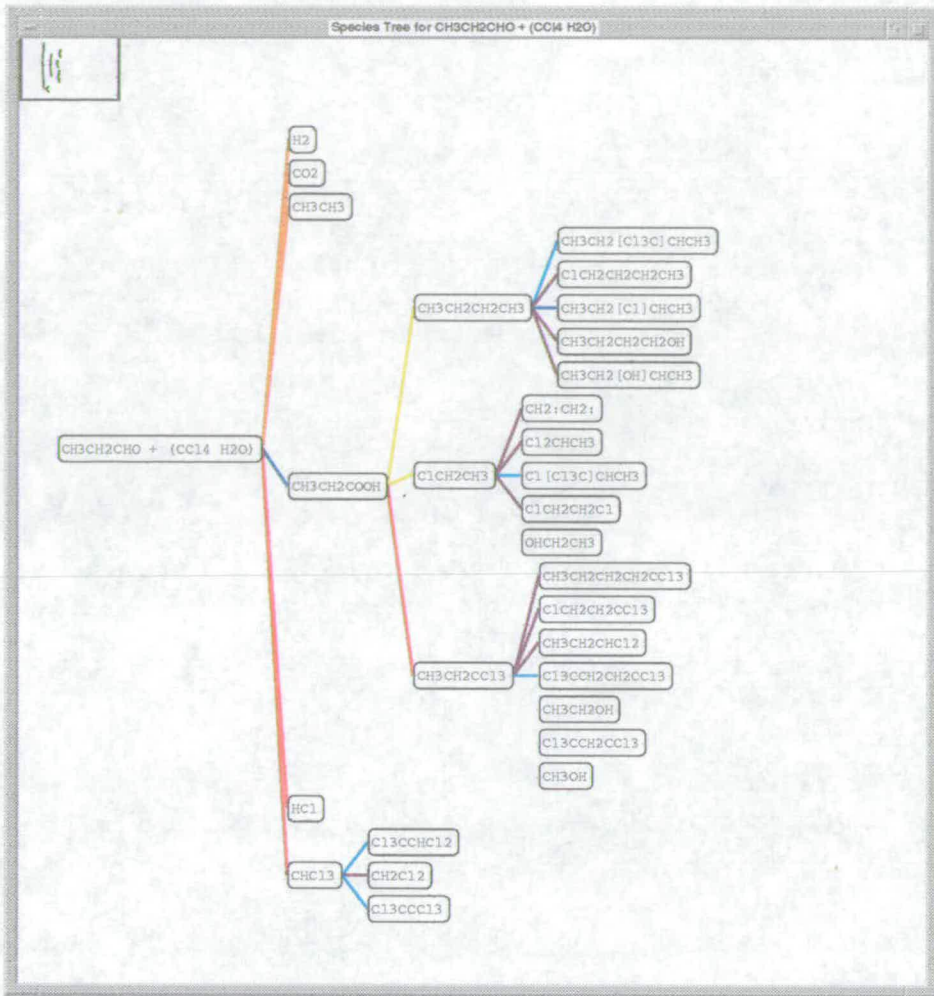
Figure 5.7: Species tree of pyrolysis reactions of oxygenated compounds

For the purpose of separation simulation, a subset of components were selected as representation of boiling point and relative volatility. The order of component boiling points is generally in corresponding with the order of the relative volatility. Therefore azeotrope is less likely than EDC purification and sharp separation is possible because of the relatively widely spread of volatility.

Table 5.6: Species formed in the pyrolysis section, their boiling points and relative volatility

Components	Boiling point, °C	Relative volatility
HCl	-85	57.61369
$CH_2=CH_2$	-103.9	25.14703
CH_3CH_3	-88.6	15.15008
Cl_2	-34.6	2.150951
CH_3Cl	-24.0	1.497758
$CH_2=CHCl(VCM)$	**-12.0**	**1.000000**
$CH_2=CHCH_2CH_3$	-3.1	0.7683953
C_4H_8	-5.0	0.3882075
CH_3CH_2Cl	11.9	0.3652721
CH_2Cl_2	39.9	9.479097E-02
CH_3CHCl_2	56.9	5.429135E-02
CCl_4	75.9	2.941843E-02
$ClCH_2CH_2Cl$ (EDC)	**83.9**	**1.325925E-02**
$CH_3CH_2CHCl_2$	87.9	1.187039E-02
$ClCH=CCl_2$	86.9	6.111355E-04
Cl_3CCCl_3	186.0	2.213554E-04
$Cl_2CHCHCl_2$	146.3	2.043232E-09

5.2.7 VCM Purification

The separation simulation for VCM purification includes three RADFRAC columns removing cracking heavies, HCl and light components and remaining EDC respectively. The flow diagram is depicted below.
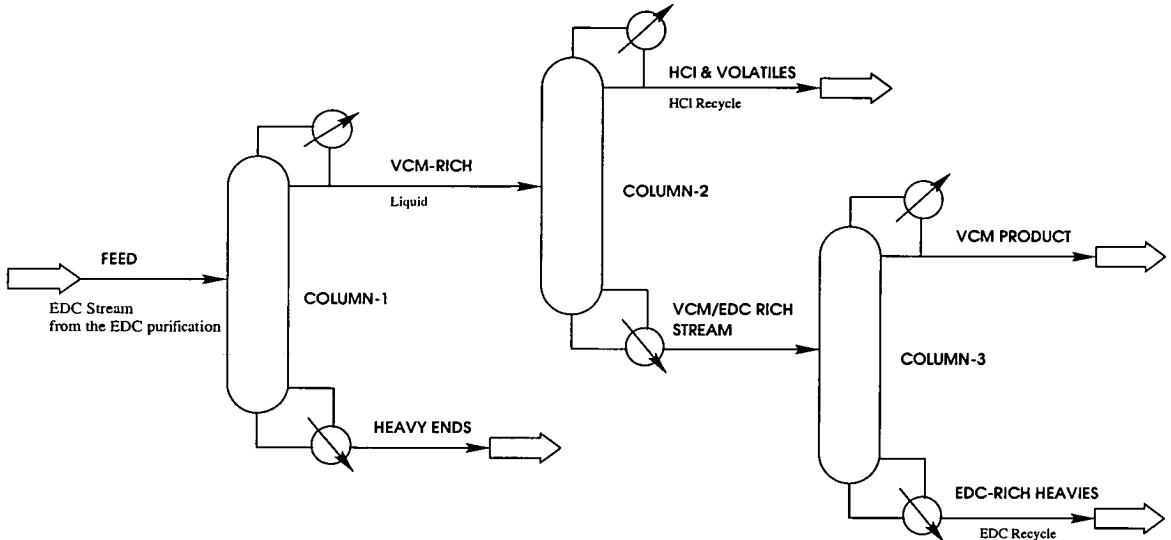
Figure 5.8: VCM Purification Simulation

Table 5.7: Results of simulation, component flow in kmol/hr

Streams	FEED	VCM-RICH	HEAVY ENDS	HCL & VOLATILES	VCM/EDC RICH	VCM PRODUCT	EDC-Rich HEAVIES
From Unit		COLUMN1	COLUMN1	COLUMN2	COLUMN2	COLUMN3	COLUMN3
To Unit	COLUMN1	COLUMN2			COLUMN3		
Temperature, $^\circ$ C	20.0	-71.0	107.1	-85.6	-22.0	-40.0	45.2
Mole flow, (kmol/hr)	34.4	34.0	0.4	10.1	23.9	20.0	3.9
HCl	10.0	10.0	trace	9.915	0.085	0.085	trace
$CH_2=CH_2$	0.1	0.1	trace	0.1	trace	trace	trace
CH_3CH_3	0.1	0.1	trace	0.085	0.015	0.015	trace
Cl_2	0.1	0.1	trace	trace	0.1	0.1	trace
CH_3Cl	0.1	0.1	trace	trace	0.1	0.1	trace
$CH_2=CHCl(VCM)$	20.0	20.0	trace	trace	20.0	19.7	0.3
$CH_2=CHCH_2CH_3$	0.1	0.1	trace	trace	0.1	< 0.001	0.1
C_4H_8	0.1	0.1	trace	trace	0.1	trace	0.1
CH_3CH_2Cl	0.1	0.1	trace	trace	0.1	trace	0.1
CH_2Cl_2	0.1	0.1	trace	trace	0.1	trace	0.1
CH_3CHCl_2	0.1	0.1	trace	trace	0.1	trace	0.1
CCl_4	0.1	0.1	trace	trace	0.1	trace	0.1
$ClCH_2CH_2Cl$ (EDC)	3.0	2.897	0.103	trace	2.897	trace	2.897
$CH_3CH_2CHCl_2$	0.1	0.003	0.097	trace	0.003	trace	0.003
$ClCH=CCl_2$	0.1	0.1	trace	trace	0.1	trace	0.1
Cl_3CCCl_3	0.1	trace	0.1				
$Cl_2CHCHCl_2$	0.1	trace	0.1				

5.2.8   Summary

1. EDC Purification

   It is clear that there are measurable amounts of material mostly chlorinated, which will be very difficult to remove from EDC. RADFRAC simulation in both separation sequences demonstrate that a number of byproducts are carried over to the pyrolysis section. The component separation in the first column of direct separation is shown in Table 5.3. EDC is taken overheads while carrying substantial amount of 'heavier' components to the second column. This effect can be explained from the list of the relative volatilites, where some of the 'heavy' components have values of 'nearly' one.

   The characteristic of the separation of the components can be justified by the types of components present in the mixture of the reactors' effluent. The presence of certain types of components together will form azeotropes. Oxygenated compounds such as alcohol and aldehyde are capable of forming three dimensional networks of strong hydrogen bonds. In the liquid classification, these compounds are included in Class I. Heavy chlorinated compounds having active hydrogen atoms are classified in Class IV. If these two compound classes are present in a mixture of liquid, then the possibility for hydrogen bond formation is greater than that of just the presence of individual compound class. The hydrogen bond denotes the degree of solubility which causes deviation from Raoult's Law correspond to differences in boiling points and thus azeotrope formation[59, 60, 61].

   The same effect is observed during further separation in the second column (Table 5) which takes EDC as the bottom product. The flow of components to the pyrolysis section shows the presence of both 'light' and 'heavy' components indicating an incomplete separation. This situation can also be justified by similar principles which apply to the components in indirect sequence where EDC is taken in the bottom product. Table 5.4 shows that a large part of 'lighter' components adhere to and carried along with EDC. In the second column where EDC is taken overhead, there are considerable amount of materials carried over to the pyrolysis section. The fraction of components carried over in the process line during EDC purification can be seen in the following figure (Fig. 5.9) using indirect sequence separation.

2. Pyrolysis Reaction

   Further analysis of the pyrolysis section shows that the components might undergo reactions with CCl_4 or other components forming new species. Most of the components formed in the pyrolysis section are heavily chlorinated which have high boiling points. Oxygenated compounds are destroyed while HCl and other gaseous products can be recovered from vinyl chloride purification section and fed back into the oxychlorinator. The remaining EDC and other 'heavier' compounds are recycled into the EDC purification. Some of the species have close boiling points relative to $ClCH_2CH_2Cl$ (ethylene dichloride). It can be seen that these species remain in the process line and are likely to accumulate.

However, vinyl chloride monomer can be recovered with high purity since the difference in the volatility is fairly large. See column 7 stream VCM PRODUCT in Table 5.7. Also see the fraction of other components in the product stream shown in Figure 5.10.

The results of the separation simulation show that sharp separation can be obtained during the purification of VCM. The amount of 'heavy' components carried overhead appear to be much less compared to that of the EDC purification. This is because the cracking process produces homogenous mixture of components largely consists of chlorinated compounds. Since there is just one single component class present, azeotrope mixture can be avoided. Therefore, deviation from ideality is unlikely. The fraction of components carried over in the process line after VCM purification can be seen in the following figure (Fig. 5.10). The magnitudes indicate that significant number of both light and heavy trace components remain after VCM purification.

3. Assessment of components carried over in the recycle streams

Figures 5.9 and 5.10 reveal fractions of components in the respective streams as a result of separation processes of EDC and VCM. In EDC purification, the feed contains very small fractions of some byproduct components such as HCl, ethanol, 1,4-hexadiene and chloroacetaldehyde. Although COLUMN-1 is intended to separate all 'light' components, but most of these components still remain with EDC in the bottom stream. The overheads carry only a smaller fraction of these components, except HCl, ethanol and water which can be separated completely. A small fraction of EDC and chloroacetaldehyde as 'heavy' components are carried over in the overhead stream, while the rest remain in the bottom stream. Most of the 'heavy' components are chlorinated such as trichloroacetaldehyde, dichloroacetaldehyde, 1,2-dichloropropane, 1,1,2-trichloroethane and also component such as isopropyl-alcohol and EDC itself. In COLUMN-2, there is only a small part of the 'heavy' components carried overhead, while the large part remain in the bottom stream. This stream is a recycle stream to an oxychlorinator together with the overhead stream from the first column. Therefore, components remain in these recycle streams are carried back into the reactor and may undergo further reactions. EDC product taken overhead from the second column contains the rest of the 'light' components and small amount of 'heavy' components. Water can be removed almost completely, which satisfies the requirement for EDC product purity (less than 10 ppm). However, the degree of purity is lower than that of the actual requirement, that is 99.5 %. This is largely due to the crude treatment process conducted before the reactor effluent stream enters the separation section. The functions of the treatments are discussed below.

In the balanced oxychlorination process considered in this study, it appears that oxygenated and other chlorinated compounds can be generated. Therefore, it is necessary for crude EDC from the oxychlorinator to undergo workup and washing and removed from oxygenated compounds. Removing these compounds may reduce EDC separator load since they can form azeotrope with the chlorinated

compounds whose effect has been discussed above. The existing VCM process is usually provided with the workup section so that high purity EDC can be obtained.

Some of the components carried in the EDC stream enter the pyrolysis section together with EDC where they undergo cracking. Most components will be heavily chlorinated, fractionated and dehydrogenated, while oxygenated compounds disappear through decomposition of the carbonyl groups. The feed to the VCM purification contains VCM, EDC and byproduct compounds such as ethylene, chlorine, cyclobutane, 1,1-dichloroethane, hexachloroethane and 1,1,2,2-tetrachloroethane. The 'heavies' produced by the cracking process has to be removed first, this is shown in COLUMN-1 where 1,1-dichloropropane, hexachloroethane, 1,1,2,2-tetrachloroethane and part of EDC except trichloro-ethylene are removed. Sharp separation can be achieved in this column. The VCM mixture taken overhead contains 'light' components, VCM and EDC. In the second column where VCM is taken in the bottom stream, a large part of HCl, ethane and ethylene can be removed, while the other components are carried along with VCM. In the third column VCM can be separated from the rest of the components containing a small amount of 'light' volatile material. EDC and other 'heavy' materials are removed from the bottom and recycled back into EDC separation section. These materials consists of 1-butene, cyclobutane, ethyl-chloride, dichloromethane, 1,1-dichloroethane, trichloroethylene and so forth.

Based on the investigations of the byproduct behaviour during EDC and VCM purification, it seems that oxychlorinator product pretreatment is necessary. Although the oxygenated compounds can be destroyed during pyrolysis, but some of them may form olefinic compounds. Decomposition product might form other heavy or carbonaceous material. Their deposit in the cracking reactor would contaminate the catalysts and thus reduce the conversion of EDC to VCM. As for the 'light' components, in order to reduce the amount of accumulation, the plant has to run an occasional purge.

Figure 5.9: Fractions of components in the process flows after EDC separation

EDC Purification

HCl	0.091	C6H6	0.006
C2H6O	0.091	**C2H4Cl2 (EDC)**	**0.597**
H2O	0.091	C2H3OCl	0.0009
C3H8O	0.04	C2HOCl3	0.0
CCl4	0.025	C2H2OCl2	0.0
C6H10	0.014	C3H4Cl2	0.0
C4H9Cl	0.012	C3H8O-1	0.0
C4H9Cl-1	0.013	C3H6Cl2	0.0
C4H10O	0.009	C2H3Cl3	0.0
C2HCl3	0.008		

LIGHT COMPONENTS TO RECYCLE

Feed stream:

HCl	0.0046
C2H6O	0.0046
H2O	0.0046
C3H8O	0.0046
CCl4	0.0046
C6H10	0.0046
C4H9Cl	0.0046
C4H9Cl-1	0.0046
C4H10O	0.0046
C2HCl3	0.0046
C6H6	0.0046
C2H4Cl2 (EDC)	**0.917**
C2H3OCl	0.0046
C2HOCl3	0.0046
C2H2OCl2	0.0046
C3H4Cl2	0.0046
C3H8O-1	0.0046
C3H6Cl2	0.0046
C2H3Cl3	0.0046

FEED

COLUMN-1
NStages = 50
RR = 3.0

EDC PRODUCT stream:

HCl	0.0	C6H6	0.0047
C2H6O	0.0	**C2H4Cl2 (EDC)**	**0.958**
H2O	0.0	C2H3OCl	0.0048
C3H8O	0.0028	C2HOCl3	0.0015
CCl4	0.0036	C2H2OCl2	0.0023
C6H10	0.0043	C3H4Cl2	0.0005
C4H9Cl	0.0044	C3H8O-1	0.0
C4H9Cl-1	0.0043	C3H6Cl2	0.0
C4H10O	0.0045	C2H3Cl3	0.0
C2HCl3	0.0046		

EDC PRODUCT

COLUMN-2
NStages = 50
RR = 3.0

EDC MIXTURE TO COLUMN-2

HCl	0.0	C6H6	0.0045
C2H6O	0.0	**C2H4Cl2 (EDC)**	**0.9344**
H2O	0.0	C2H3OCl	0.0048
C3H8O	0.0027	C2HOCl3	0.0048
CCl4	0.0035	C2H2OCl2	0.0048
C6H10	0.0041	C3H4Cl2	0.0048
C4H9Cl	0.0042	C3H8O-1	0.0048
C4H9Cl-1	0.0042	C3H6Cl2	0.0048
C4H10O	0.0044	C2H3Cl3	0.0048
C2HCl3	0.0044		

HEAVIES TO RECYCLE

HCl	0.0	C6H6	0.0
C2H6O	0.0	**C2H4Cl2 (EDC)**	**0.34**
H2O	0.0	C2H3OCl	0.0038
C3H8O	0.0	C2HOCl3	0.088
CCl4	0.0	C2H2OCl2	0.068
C6H10	0.0	C3H4Cl2	0.124
C4H9Cl	0.0	C3H8O-1	0.125
C4H9Cl-1	0.0	C3H6Cl2	0.125
C4H10O	0.0	C2H3Cl3	0.125
C2HCl3	0.0		

COMPONENT FORMULAE AND NAME

HCl	Hydrogen chloride
C2H6O	Ethanol
H2O	Water
C3H8O	1-Propanol
CCl4	Carbon tetrachloride
C6H10	1,4 Hexadiene
C4H9Cl	2-Chlorobutane
C4H9Cl-1	1-Chlorobutane
C4H10O	2-Butanol
C2HCl3	Trichloroethylene
C6H6	Benzene
C2H4Cl2	**1,2-Dichloroethane**
C2H3OCl	Chloroacetaldehyde
C2HOCl3	Trichloroacetaldehyde
C2H2OCl2	Dichloroacetaldehyde
C3H4Cl2	2,3-Dichloropropene
C3H8O-1	Isopropyl-alcohol
C3H6Cl2	1,2-Dichloropropane
C2H3Cl3	1,1,2-Trichloroethane

VCM Purification

Figure 5.10: Fractions of components in the process flows after VCM Purification

HCl	0.294	CH2Cl2	0.0029
C2H4	0.0029	C2H4Cl2	0.0029
C2H6	0.0029	CCl4	0.0029
Cl2	0.0029	C2H4Cl2-1	0.0852
CH3Cl	0.0029	C3H6Cl2	0.0029
C2H3Cl	0.588	C2HCl3	0.0029
C4H8-1	0.0029	C2Cl6	0.0
C4H8	0.0029	C2H2Cl4	0.0
C2H5Cl	0.0029		

HCl	0.982	CH2Cl2	0.0
C2H4	0.0099	C2H4Cl2	0.0
C2H6	0.0084	CCl4	0.0
Cl2	0.0	C2H4Cl2-1	0.0
CH3Cl	0.0	C3H6Cl2	0.0
C2H3Cl	0.0	C2HCl3	0.0
C4H8-1	0.0	C2Cl6	0.0
C4H8	0.0	C2H2Cl4	0.0
C2H5Cl	0.0		

HCL & VOLATILITES

VCM MIXTURE TO COLUMN-2

HCl	0.0042	CH2Cl2	0.0
C2H4	0.0	C2H4Cl2	0.0
C2H6	0.0008	CCl4	0.0
Cl2	0.005	C2H4Cl2-1	0.0
CH3Cl	0.005	C3H6Cl2	0.0
C2H3Cl	0.985	C2HCl3	0.0
C4H8-1	0.0	C2Cl6	0.0
C4H8	0.0	C2H2Cl4	0.0
C2H5Cl	0.0		

HCl	0.291		
C2H4	0.0029		
C2H6	0.0029		
Cl2	0.0029		
CH3Cl	0.0029		
C2H3Cl (VCM)	0.5814		
C4H8-1	0.0029		
C4H8	0.0029		
C2H5Cl	0.0029		
CH2Cl2	0.0029		
C2H4Cl2	0.0029		
CCl4	0.0029		
C2H4Cl2-1 (EDC)	0.087		
C3H6Cl2	0.0029		
C2HCl3	0.0029		
C2Cl6	0.0029		
C2H2Cl4	0.0029		

FEED

COLUMN-1 NStage = 50 RR = 5.0

COLUMN-2 NStage = 50 RR = 5.0

VCM PRODUCT

VCM TO BE PURIFIED

COLUMN-3 NStage = 50 RR = 5.0

HEAVIES FOR RECYCLE

EDC & HEAVIES FOR RECYCLE

HCl	0.0	CH2Cl2	0.0
C2H4	0.0	C2H4Cl2	0.0
C2H6	0.0	CCl4	0.0
Cl2	0.0	C2H4Cl2-1	0.2575
CH3Cl	0.0	C3H6Cl2	0.242
C2H3Cl	0.0	C2HCl3	0.0
C4H8-1	0.0	C2Cl6	0.25
C4H8	0.0	C2H2Cl4	0.25
C2H5Cl	0.0		

HCl	0.0036	CH2Cl2	0.0042
C2H4	0.0	C2H4Cl2	0.0042
C2H6	0.0006	CCl4	0.0042
Cl2	0.0042	C2H4Cl2-1	0.1212
CH3Cl	0.0042	C3H6Cl2	0.0001
C2H3Cl	0.8368	C2HCl3	0.0042
C4H8-1	0.0042	C2Cl6	0.0
C4H8	0.0042	C2H2Cl4	0.0
C2H5Cl	0.0042		

HCl	0.0	CH2Cl2	0.0256
C2H4	0.0	C2H4Cl2	0.0256
C2H6	0.0	CCl4	0.0256
Cl2	0.0	C2H4Cl2-1	0.7428
CH3Cl	0.0	C3H6Cl2	0.0008
C2H3Cl	0.0769	C2HCl3	0.0256
C4H8-1	0.0256	C2Cl6	0.0
C4H8	0.0256	C2H2Cl4	0.0
C2H5Cl	0.0256		

COMPONENT FORMULAE AND NAME

HCl	Hydrogen chloride
C2H4	Ethylene
C2H6	Ethane
Cl2	Chlorine
CH3Cl	Methyl-chloride
C2H3Cl	Vinyl-chloride
C4H8-1	1-Butene
C4H8	Cyclobutane
C2H5Cl	Ethyl-chloride
CH2Cl2	Dichloromethane
C2H4Cl2	1,1-Dichlorothane
CCl4	Carbon tetrachloride
C2H4Cl2-1	1,2-Dichloroethane
C3H6Cl2	1,1-Dichloropropane
C2HCl3	Trichloroethylene
C2Cl6	Hexachloroethane
C2H2Cl4	1,1,2,2-Tetrachloroethane

5.3 The R-134a Process

5.3.1 Reaction Analysis

Plant Chemistry

R-134a (1,1,1,2-tetrafluoroethane; (F_3CCH_2F) is manufactured by reacting trichloro-ethene ($Cl_2C=CH_2Cl$) with hydrogen fluoride (HF). The main reactions consist of two steps, the production of R-133a and the conversion of R-133a to R-134a as shown below:

1. $Cl_2C=CH_2Cl + 3HF \rightarrow F_3CCH_2Cl + 2\ HCl$

2. $F_3CCH_2Cl + HF \rightarrow F_3CCH_2F + HCl$

Figure 5.11 illustrates the process block flowsheet.
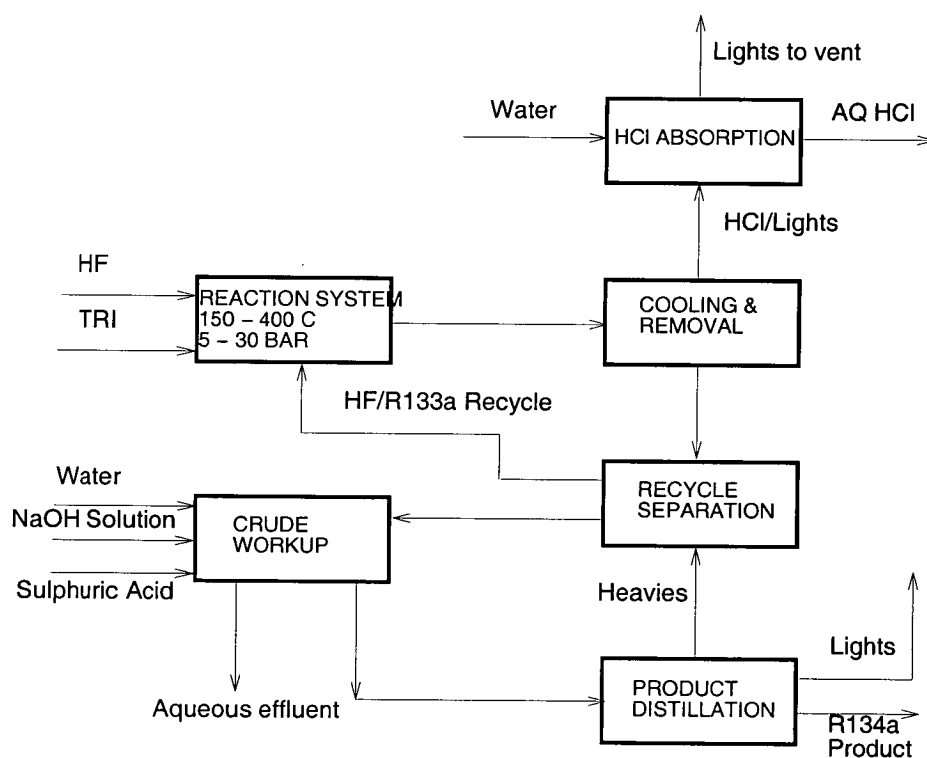
Figure 5.11: R134a Process Flow

Chemistry Principles

The production of R-134a is carried out by electrophilic addition towards olefin, substitution of halogen and elimination. Electrophilic addition causes double bond cleavage providing intermediate carbonium ion, such as CH_3C^+. The carbonium ion is stabilized by alkyl groups attached to it and attracts nucleophilic agents to add. Nucleophilic

agents are those of halogens, hydrogen, nitrogen, sulphur, oxygen and carbon. Substitution reaction involves the replacement of one group by another in one of three ways: synchronous substitution, elimination followed by addition and/or addition followed by elimination. Since the raw materials comprise olefinic with halogenized structures, the reaction mechanisms are built up according to the above principles. The following sections discuss species and reactions generated by the program.

5.3.2 Results and Analysis

The main initial species consist of 1,1,2-trichloroethene (tri), hydrogen fluoride and water. The HF feedstock contains impurities such as H_2SO_4, AsF_3 and AsF_5. Principal impurities in tri are ethylene dichloride, perchlorethylene, water, bromodichloromethane, trichloroethane, carbon tetrachloride, vinylidene chloride and chloroform. The reaction system has 150-400 °C operating temperature and 5-30 bar. The initial reaction which is considered as **Level 1** produces 7 surviving species generated by the addition and substitution reactions. The reactions developed by the program are shown below :

LEVEL 1

1. $2\ Cl_2C=CHCl \rightarrow Cl_2C=CCl_2 + Cl_2C=CH_2$
   $\Delta G_{298K} = -0.93 (kJ/mol)$

2. $2\ Cl_2C=CHCl + HF \rightarrow Cl_2CH[F]CHCl$
   $\Delta G_{298K} = 2.04 (kJ/mol)$

3. $2\ Cl_2C=CHCl + HF \rightarrow Cl_2[F]CCH_2Cl$
   $\Delta G_{298K} = 9.76 (kJ/mol)$

4. $2\ Cl_2C=CHCl + HF \rightarrow FCH=CCl_2 + HCl$
   $\Delta G_{298K} = -4.81 (kJ/mol)$

5. $2\ Cl_2C=CHCl + HF \rightarrow Cl[F]C=CHCl + HCl$
   $\Delta G_{298K} = -4.81 (kJ/mol)$

The surviving species are as follows : $Cl_2C=CCl_2$, $Cl_2C=CH_2$, $Cl_2CH[F]CHCl$, $FCH=CCl_2$, HCl, $Cl_2[F]CCH_2Cl$, $Cl[F]C=CHCl$. The tree diagram of the species formation is presented in Figure 5.12. The figure shows that R-134a could be developed through routes different from that of the plant chemistry. It appears that the production of 1,1,1,2-tetrafluoroethane could follow several reaction routes. However the program is designed to expand the most negative free energy change, i.e. reaction 5. At **Level 2**, $Cl[F]C=CHCl$ produced one surviving species, i.e. $F_2C=CHCl$, which forks into three branches at **Level 3**, i.e. the formation of 2-chloro 1,1,1-trifluoroethane (R133a), 1-chloro,1,1,2-fluoroethane and 1,1,2-trifluoroethene route. This program generates R134a through 1,1,2-trifluoroethene. Subsequent substitution of chlorine atom occurs first before final electrophilic addition at the olefin bond. R133a is formed through the reaction of 1-chloro,2,2-fluoroethene and HF.
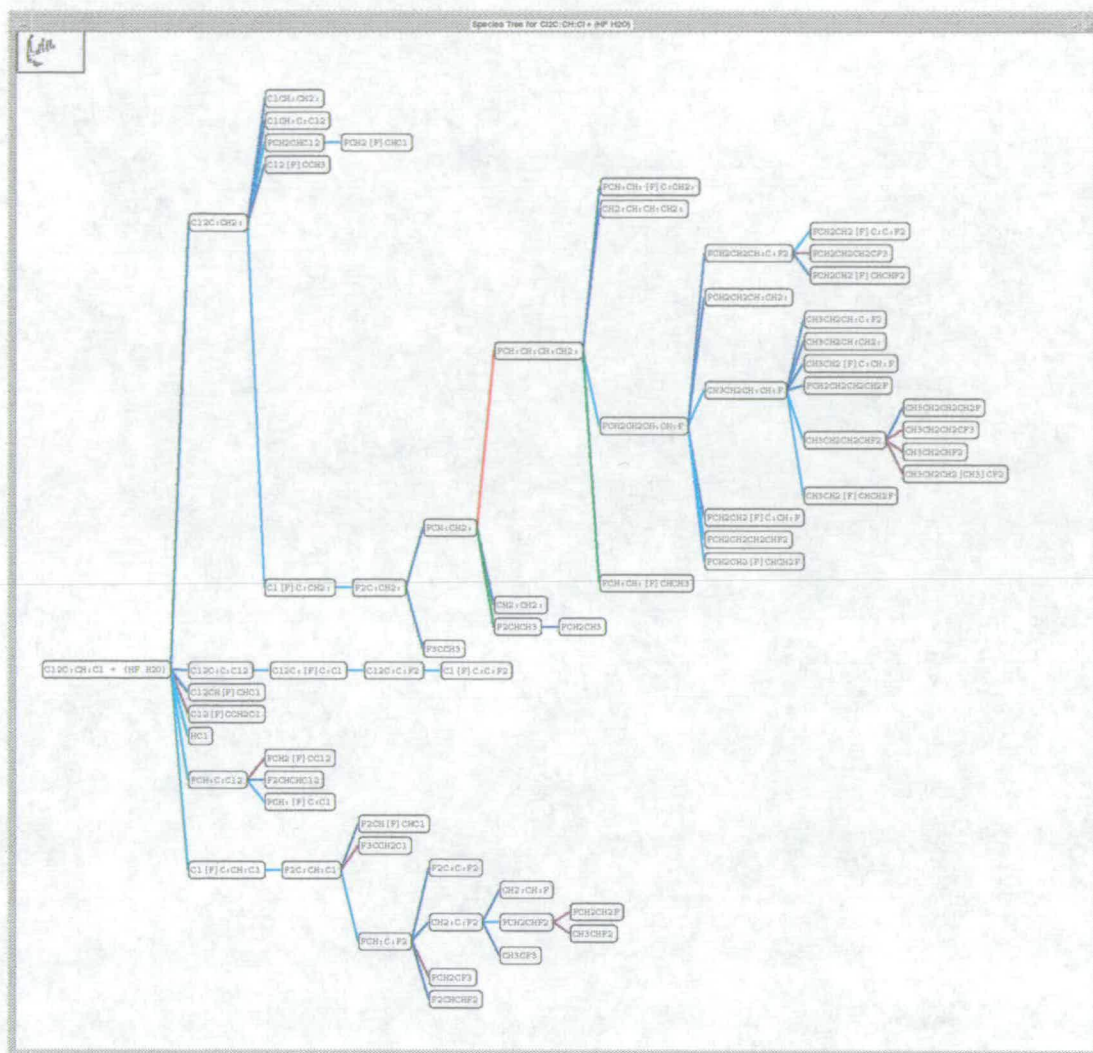
Figure 5.12: The tree diagram of species formation in R-134a Process

LEVEL 3

1. $F_2C=CHCl + HF \rightarrow F_2CH[F]CHCl$
   $\Delta G_{298K} = 2.04 (kJ/mol)$

2. $F_2C=CHCl + HF \rightarrow F_3CCH_2Cl$
   $\Delta G_{298K} = 9.76 (kJ/mol)$

3. $F_2C=CHCl + HF \rightarrow HCl + FCH=CF_2$
   $\Delta G_{298K} = -4.81 (kJ/mol)$

LEVEL 4

Level 4 is the expansion of reaction 3 in **Level 3** generating three reactions, as follows:

1. $2\ FCH{=}CF_2 \rightarrow F_2C{=}CF_2 + CH_2{=}CF_2$
   $\Delta G_{298K} = -0.93 (kJ/mol)$

2. $FCH{=}CF_2 + HF \rightarrow FCH_2CF_3$
   $\Delta G_{298K} = 9.76 (kJ/mol)$

3. $FCH{=}CF_2 + HF \rightarrow F_2CHCHF_2$
   $\Delta G_{298K} = 2.04 (kJ/mol)$

The program chose to expand reaction 3 in **Level 3** instead of reaction 2 in **Level 3** which results in the formation of R133a. This is due to its more positive free energy change. Although subsequently, the reaction free energy change of R133a to R134a is negative as shown below.

1. $F_3CCH_2Cl + HF \rightarrow FCH_2CF_3 + HCl$
   $\Delta G_{298K} = -4.81 (kJ/mol)$

It is evident that the conversion of $-CH_2Cl$ group to $-CH_2F$ group is difficult and would require expensive fluorinating agent[62]. This program selects nodes which are produced from reactions having the most negative free energy change. Therefore, the route taken by the program is different from that of the plant chemistry. The electrophilic addition to olephine requires slightly positive free energy change as shown in reaction 2 at **Level 3** and reaction 2 at **Level 4**. From the list of reactions it can be seen that substitution reactions have more negative free energy change than the hydrogen addition. Therefore, substitution occurs first followed by addition.

However, this is not so in the real process where the product is formed through the formation of R133a. The synthesis of R-134a can be a complex reaction network as shown in a paper written by Manzer[62]. He presented the potential routes from four different starting species, i.e. tetrachloroethylene, tricholoroethylene, vinyl chloride and tetrachloroethane. The network generated from four different raw materials is depicted in diagram 5.13. When using TCE (as used in this case study), there are two routes that can be followed, i.e. R123 and R133a which are formed by hydrogen (H^+) addition. Therefore, in reality, double bond cleavage followed by hydrogen addition occurs first before further chlorine substitution. This is largely due to the selectivity towards the product species created by catalysts.

5.3.3   List of byproducts

In addition to those impurities found in the chemical process, such as ethylene dichloride, perchloroethylene and carbon tetrachloride, a number of other species have been generated by the program. Most of these species are chlorinated and fluorinated. The following table presents some of the species generated by the program.

CCl2=CCl2
PCE

CCl2=CHCl
TCE

CF3CHCl2
R123

CF2ClCCl2F
R113

CF2ClCF2Cl
R114

CF3CH2Cl
R133a

CF3CCl3
R133a

CF3CFCl2
R114a

CF3CHFCl
R124

CF2=CFCl
CTFE

CClF2CH2F
R133b

CF3CH2F
R134a

CCl2=CHF
R1121

CF2=CFH
R1123

CHClFCHCl2
R131

CF3CH3
R143a

CF2HCF2H
R134

CH2=CCl2
R1130

CF2=CH2
R1132
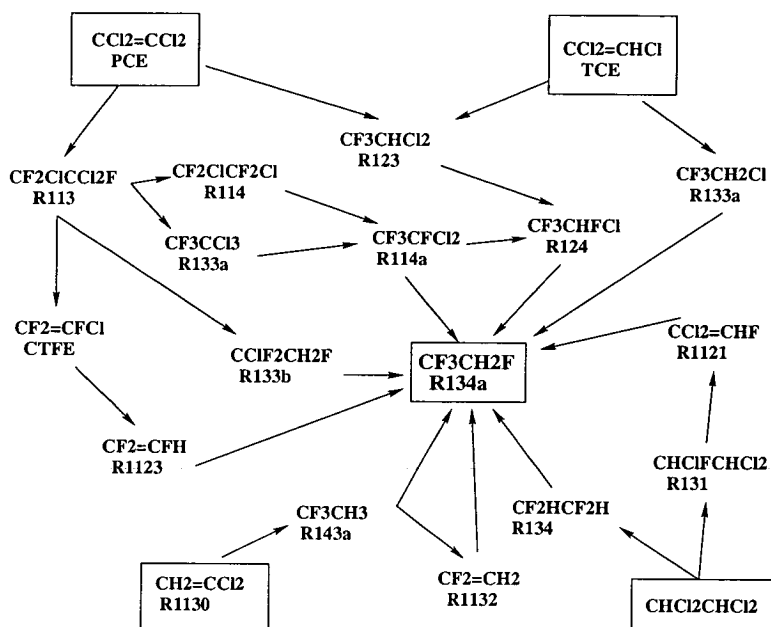
CHCl2CHCl2

Figure 5.13: Reaction network showing potential routes to R-134a (Manzer [62])

Table 5.8: List of species generated by the program

$Cl_2C=CCl_2$	$Cl_2C=CH_2$	$Cl_2CH[F]CHCl$
$FCH=CCl_2$	HCl	$Cl[F]C=CHCl$
FCH_2CHCl_2	$Cl_2[F]CCH_3$	$ClCH=CCl_2$
$FCH_2[F]CCl_2$	$FCH=[F]CCl$	$Cl[F]C=CH_2$
$F_2CH[F]CHCl$	$F_2C=CF_2$	$CH_2=CF_2$
F_2CHCHF_2	$CH_2=CHF$	FCH_2CHF_2
CH_3CF_3	FCH_2CH_2F	CH_3CHF_2
$CH_2=CH_2$	C_4H_8	$CH3CHCl_2$
CH_3CH_3	CH_2Cl_2	$CHCl_3$
FCH_2CHF_2	CH_3CF_3	CH_3CCl_3
$ClCH_2CH_2Cl$	$Cl_2CHCHCl_2$	$ClCH_2CHCl_2$
$ClCH=CH_2$	CH_3CH_2Cl	$CH_2=CHCH_2CH_3$
$FCH=CHCH=CH_2$	F_2CHCF_3	FCH_2CHCl_2

Species having close boiling points to R-134a are listed in the following table. The boiling point of R-134a is -26.4 °C (246.7 K). Most chlorinated products have high boiling points, therefore are not included the list, while most fluorinated products have low boiling points which are closer to the key component.

5.3.4 R-134a Purification

R-134a purification process comprises several stages : cooling and light removal, recycle separation, crude workup and product distillation. HCl and light components are removed by partial distillation and cooling the off-gas outflow of the reactor near ambient temperature. Recycled products such as HF and R133a are separated at the recycle separation section. Before entering product distillation, the mixture undergoes washing treatment with water, NaOH solution and sulphuric acid to remove oxidized components and other 'undesired' precipitation from the vapourised crude product. Clean product is then sent to a distillation column to remove the lights and the heavies and obtain pure R-134a as the desired product.

To simulate the behaviour of the components in the separation section, RADFRAC simulation from ASPEN is used. In this simulation task, the quantity of the main component, i.e R-134a is given in a large amount compared to other components. See Table 5.10 for feed composition. It is assumed that other components are present in trace quantities, except HF and R-133a which are given in slightly bigger quantities since they are present due to incomplete reaction. The flow of the separation simulation can be seen in Figure 5.14. The results are presented in Table 5.10.

5.3.5   Relative Volatility

Table 5.9: List of species generated by the program

Component	Relative volatility
$CH_2=CH_2$	12.58323
$FCH=CHF$	7.695391
CH_3CH_3	7.473776
HCl	6.540590
F_2CHCF_3	2.346038
CH_3CF_3	2.120447
CH_3CH_2F	1.408923
F_3CCH_2F	1.000000
F_2CHCHF_2	0.8233484
$F_2C=CHCl$ 4	0.7092946
$ClCH=CH_2$	0.5794520
$CH_2=CHCH_2CH_3$	0.4461587
C_4H_8	0.2385919
CH_3CH_2Cl	0.2097237
F_3CCH_2Cl	0.1119835
$Cl_2C=CH_2$	9.628934E-02
HF	8.721004E-02
$CH_3[CH_3]CHCl$	8.274888E-02
CH_2Cl_2	6.446428E-02
$ClCH_2CH_2Cl$	3.254716E-02
$CHCl_3$	2.767826E-02
CH_3CCl_3	1.655806E-02
CCl_4	1.545901E-02
$CH_3CH_2CHCl_2$	8.069773E-02
Cl_3CCH_2F	6.693752E-03
H_2O	2.752804E-03

5.3.6   RADFRAC Simulation

26 components have been selected for the purpose of separation simulation. Some of these components have close boiling point to the key component, i.e. F_3CCH_2F. The results show that, in the recycle separation where the 'heavy' key component is F_3CCH_2Cl, a sharp separation occurs providing discrete separation between the lights and the heavies. Trace amount of light components appear in the bottom product, and likewise for the heavy components in the top product. The second column involving product separation also exhibits a sharp separation where the overhead section carries all the light components and the bottom section carries the heavy components.

The study on side reaction generation of R-134a process indicates the generation of chlorinated and fluorinated components which can be categorized in class IV and II respectively. The presence of these two classes together forms limited solubility, that is

Figure 5.14: R-134a Purification Simulation

the magnitude of deviation in Raoult's law is relatively small. The present of water in the raw material may propagate reaction with hydroxyl, however, such components do not prevail since the addition of OH group requires large free energy change. Therefore, azetrope mixture might form to a very limited extent and thus 'undesired' components seem to be separable from the main product. However, material accumulation in the process line cannot be minimized or avoided since these components are carried back to the reactor.

5.3.7 Assessment of Components Carried Over in the Recycle Streams

The results shown in Figure 5.15 indicate that the recycle flow to HF/R-133a reactor contains significant number of byproducts. The feed from the reactor consists of components such as ethylene, ethane, pentafluoroethane, 1-butene, ethylchloride, chloroform, 1,1,1-trichlorofluoroethane and so on. The main products of 1,1,1,2-tetrafluoroethane (R134a), 2-chloro-1,1,1-trifluoroethane (R133a) and unreacted hydrogen fluoride occur in a considerable large amount compared to the other byproducts. In the first recycle separation column, HF and R133a are separated, taken as the bottom product and recycled back into the reactor. They carry the entire 'heavy' components with them into the reactor which might undergo further reactions. Most of the 'heavy' components are chlorinated such as 1,1-dichloroethane, isopropyl-chloride, 1,1-dichloroethylene and carbon tetrachloride. If these components

are allowed to react further then more possibilities can be generated. Species with longer chains are produced as a result of coupling, further chlorination or fluorination may also occur. For an illustration, 9 components have been selected and the results can be seen in the following diagram (Fig. 5.16). Therefore, workup section and purging are required to avoid unnecessary load in the reactor and the separation units.

In the overhead stream, 1,1,1,2-tetrafluoroethane (R134a) carries other 'light' components with it, such as ethylene, ethane, 1,1-difluoroethylene, hydrogen chloride, ethyl fluoride and so forth. Most of these components are fluorinated. In the second column, R134a is purified and taken overhead. The 'heavy' components, relative to R134a as the light key, consist of 1,butene, cyclobutane and ethyl chloride are separated and recycled back to the first column. In the first column, where HF is the heavy key component, the relative volatility of the recycled three components lie between HF and R134a. Therefore, it is likely that the recycle would cause their continuous presence in the process line and may accumulate. However, since the outlet of the recycle separation column undergo workup, then some of them could be washed away and thus reducing their occurence in the process line. Before entering the reactor once again, HF/R133a could be purified from the 'heavies'. These could be removed during crude treatment.

The third column which purifies R134a from other 'light' material results in the removal of most of the 'lights' as mentioned above. The 'light' components will be incinerated and therefore will not accumulate. The product stream contains a high R134a purity with a trace amount of ethyl fluoride, 1,1,2,2-tetrafluoroethane, vinylchloride and few others. These components have very close boiling points and belong to two different classes and therefore difficult to remove completely. Chlorinated compounds having two or three chlorine atoms belong to Class IV that is liquids composed of molecules with active hydrogen but no donor atom. Fluorinated compounds belong to Class II that is compounds with molecules containing both active hydrogen atoms and donor atoms (i.e. oxygen, nitrogen and fluorine). The mixing of these two classes together results in limited solubility, which means limited formation of hydrogen bond[59]. The formation of azeotrope depends on the extent of the solubility and thus determine the magnitude of deviation in Raoult's law. Therefore, some fluorinated and chlorinated compounds still remain in the product stream.

Table 5.10: Results of simulation, component flow in kmol/hr

Streams	Feed	Light Material	R134-Rich	HF-R133A	LIGHT ENDS	R134A PRODUCT	HEAVIES
From Unit		REC COL	REC COL	REC COL	PRO COL	PRO COL	PRO COL
To Unit	REC COL	PRO COL	PRO COL				
Temperature, $^\circ$ C	20.0	-26.7	-26.7	29.5	-28.6	-28.6	4.2
Mole flow, kmol/hr	57.3	15.65	15.65	26.0	1.55	29.45	0.3
$CH_2=CH_2$	0.1	0.095	0.005	trace	0.049	0.051	trace
$FCH=CHF$	0.1	0.092	0.008	trace	0.036	0.064	trace
CH_3CH_3	0.1	0.091	0.009	trace	0.034	0.066	trace
HCl	0.1	0.090	0.01	trace	0.031	0.069	trace
F_2CHCF_3	0.1	0.072	0.028	trace	0.01 1	0.089	trace
CH_3CF_3	0.1	0.071	0.029	trace	0.011	0.089	trace
CH_3CH_2F	0.1	0.061	0.039	trace	0.007	0.093	trace
F_3CCH_2F	30.0	14.888	15.112	trace	1.361	28.639	trace
F_2CHCHF_2	0.1	0.046	0.054	trace	0.004	0.096	trace
$F_2C=CHCl$	0.1	0.041	0.059	trace	0.003	0.097	trace
$ClCH=CH_2$	0.1	0.037	0.063	trace	0.003	0.097	< 0.001
$CH_2=CHCH_2CH_3$	0.1	0.031	0.069	trace	trace	< 0.001	0.1
C_4H_8	0.1	0.018	0.082	trace	trace	trace	0.1
CH_3CH_2Cl	0.1	0.015	0.085	< 0.001	trace	trace	0.1
F_3CCH_2Cl	20.0	trace	< 0.001	20.0	trace	trace	< 0.001
$Cl_2C=CH_2$	0.1	trace	trace	0.1	trace	trace	trace
HF	5.0	trace	trace	5.0	trace	trace	trace
$CH_3[CH_3]CHCl$	0.1	trace	trace	0.1	trace	trace	trace
CH_2Cl_2	0.1	trace	trace	0.1	trace	trace	trace
$ClCH_2CH_2Cl$	0.1	trace	trace	0.1			
$CHCl_3$	0.1	trace	trace	0.1			
CH_3CCl_3	0.1	trace	trace	0.1			
CCl_4	0.1	trace	trace	0.1			
$CH_3CH_2CHCl_2$	0.1	trace	trace	0.1			
Cl_3CCH_2F	0.1	trace	trace	0.1			
H_2O	0.1	trace	trace	0.1			

Figure 5.15: Fractions of components in the process flows after R134a Purification

LIGHTS / R134 MIX

C2H4	0.0061 / 0.00032	C2H5Cl	0.00096 / 0.00543
C2H6	0.0059 / 0.00051	C2H2ClF3	0.0 / 0.0
C2H2F2	0.0058 / 0.00058	C2H2Cl2	0.0 / 0.0
HCl	0.0058 / 0.00064	HF	0.0 / 0.0
C2HF5	0.0046 / 0.00179	C3H7Cl	0.0 / 0.0
C2H3F3	0.0045 / 0.00185	CH2Cl2	0.0 / 0.0
C2H5F	0.0039 / 0.00249	C2H4Cl2	0.0 / 0.0
C2H2F4	0.9513 / 0.9656	CHCl3	0.0 / 0.0
C2H2F4-1	0.0029 / 0.00345	C2H3Cl3	0.0 / 0.0
C2HClF2	0.0026 / 0.00377	CCl4	0.0 / 0.0
C2H3Cl	0.0024 / 0.00403	C3H6Cl2	0.0 / 0.0
C4H8	0.0019 / 0.0044	C2H2Cl3F	0.0 / 0.0
C4H8-1	0.0115 / 0.00524	H2O	0.0 / 0.0

LIGHTS / R134

C2H4	0.0316 / 0.0017	C2H5Cl	0.0 / 0.0
C2H6	0.0232 / 0.0022	C2H2ClF3	0.0 / 0.0
C2H2F2	0.0219 / 0.0022	C2H2Cl2	0.0 / 0.0
HCl	0.020 / 0.0023	HF	0.0 / 0.0
C2HF5	0.0071 / 0.003	C3H7Cl	0.0 / 0.0
C2H3F3	0.0071 / 0.003	CH2Cl2	0.0 / 0.0
C2H5F	0.0045 / 0.032	C2H4Cl2	0.0 / 0.0
C2H2F4	0.8774 / 0.9725	CHCl3	0.0 / 0.0
C2H2F4-1	0.0026 / 0.0033	C2H3Cl3	0.0 / 0.0
C2HClF2	0.0019 / 0.0033	CCl4	0.0 / 0.0
C2H3Cl	0.0019 / 0.0033	C3H6Cl2	0.0 / 0.0
C4H8	0.0 / 0.0	C2H2Cl3F	0.0 / 0.0
C4H8-1	0.0 / 0.0	H2O	0.0 / 0.0

LIGHTS / R134

C2H4	0.1	C2H5Cl	0.0
C2H6	0.1	C2H2ClF3	0.0
C2H2F2	0.1	C2H2Cl2	0.0
HCl	0.1	HF	0.0
C2HF5	0.03	C3H7Cl	0.0
C2H3F3	0.028	CH2Cl2	0.0
C2H5F	0.013	C2H4Cl2	0.0
C2H2F4	0.528	CHCl3	0.0
C2H2F4-1	0.0	C2H3Cl3	0.0
C2HClF2	0.0	CCl4	0.0
C2H3Cl	0.0	C3H6Cl2	0.0
C4H8	0.0	C2H2Cl3F	0.0
C4H8-1	0.0	H2O	0.0

FEED

C2H4	0.00175
C2H6	0.00175
C2H2F2	0.00175
HCl	0.00175
C2HF5	0.00175
C2H3F3	0.00175
C2H5F	0.00175
C2H2F4	0.524
C2H2F4-1	0.00175
C2HClF2	0.00175
C2H3Cl	0.00175
C4H8	0.00175
C4H8-1	0.00175
C2H5Cl	0.00175
C2H2ClF3	0.349
C2H2Cl2	0.00175
HF	0.0873
C3H7Cl	0.00175
CH2Cl2	0.00175
C2H4Cl2	0.00175
CHCl3	0.00175
C2H3Cl3	0.00175
CCl4	0.00175
C3H6Cl2	0.00175
C2H2Cl3F	0.00175
H2O	0.00175

RECYCLE SEPARATION COLUMN

LIGHT MATERIAL

R134 MIXTURE

HF / R133A MIXTURE TO REACTION SYSTEM

R134 PURIFICATION COLUMN-1

LIGHTS

R134

HEAVY MATERIAL TO RECYCLE

LIGHT MATERIAL TO INCINERATION

R134 PURIFICATION COLUMN-2

PURE R134

C2H4	0.0	C2H5Cl	0.33
C2H6	0.0	C2H2ClF3	0.0
C2H2F2	0.0	C2H2Cl2	0.0
HCl	0.0	HF	0.0
C2HF5	0.0	C3H7Cl	0.0
C2H3F3	0.0	CH2Cl2	0.0
C2H5F	0.0	C2H4Cl2	0.0
C2H2F4	0.0	CHCl3	0.0
C2H2F4-1	0.0	C2H3Cl3	0.0
C2HClF2	0.0	CCl4	0.0
C2H3Cl	0.0	C3H6Cl2	0.0
C4H8	0.33	C2H2Cl3F	0.0
C4H8-1	0.33	H2O	0.0

C2H4	0.0	C2H5Cl	0.0
C2H6	0.0	C2H2ClF3	0.769
C2H2F2	0.0	C2H2Cl2	0.0039
HCl	0.0	HF	0.192
C2HF5	0.0	C3H7Cl	0.0039
C2H3F3	0.0	CH2Cl2	0.0039
C2H5F	0.0	C2H4Cl2	0.0039
C2H2F4	0.0	CHCl3	0.0039
C2H2F4-1	0.0	C2H3Cl3	0.0039
C2HClF2	0.0	CCl4	0.0039
C2H3Cl	0.0	C3H6Cl2	0.0039
C4H8	0.0	C2H2Cl3F	0.0039
C4H8-1	0.0	H2O	0.0039

C2H4	0.0	C2H5Cl	0.0
C2H6	0.0	C2H2ClF3	0.0
C2H2F2	0.0	C2H2Cl2	0.0
HCl	0.0	HF	0.0
C2HF5	0.0023	C3H7Cl	0.0
C2H3F3	0.0024	CH2Cl2	0.0
C2H5F	0.0029	C2H4Cl2	0.0
C2H2F4	0.9824	CHCl3	0.0
C2H2F4-1	0.0033	C2H3Cl3	0.0
C2HClF2	0.0033	CCl4	0.0
C2H3Cl	0.0033	C3H6Cl2	0.0
C4H8	0.0	C2H2Cl3F	0.0
C4H8-1	0.0	H2O	0.0

NOMENCLATURE

C2H4	ETHYLENE
C2H6	ETHANE
C2H2F2	1,1-DIFLUOROETHYLENE
HCl	HYDROGEN CHLORIDE
C2HF5	PENTAFLUOROETHANE
C2H3F3	1,1,1-TRIFLUOROETHANE
C2H5F	ETHYL-FLUORIDE
C2H2F4	1,1,1,2-TETRAFLUOROETHANE
C2H2F4-1	1,1,2,2-TETRAFLUOROETHANE
C2HClF2	2-CHLORO-1,1-DIFLUOROETHYLENE
C2H3Cl	VINYL-CHLORIDE
C4H8	1-BUTENE
C4H8-1	CYCLOBUTANE
C2H5Cl	ETHYL-CHLORIDE
C2H2ClF3	1-CHLORO-2,2,2-TRIFLUOROETHANE
C2H2Cl2	1,1-DICHLOROETHYLENE
HF	HYDROGEN-FLUORIDE
C3H7Cl	ISOPROPYL-CHLORIDE
CH2Cl2	DICHLOROMETHANE
C2H4Cl2	1,1-DICHLOROETHANE
CHCl3	CHLOROFORM
C2H3Cl3	1,1,1-TRICHLOROETHANE
CCl4	CARBON-TETRACHLORIDE
C3H6Cl2	1,1-DICHLOROPROPANE
C2H2Cl3F	1,1,1-TRICHLOROFLUOROETHANE
H2O	WATER

Figure 5.16: Assessment for further species generation

5.3.8   The Effect of Impurities in the Feedstock

The feedstock contains impurities which might react with the main species. The effect of the presence of sulfuric acid in the feedstock was studied and the results are presented in Figure 5.17. From the small number of sulfuric components that were generated, it can be seen that reactions between structures having double bond and halogens with sulfuric radicals were difficult. Sulfuric components were generated mostly from the reaction of alkanes, such as : $CH_3(SO_2)OH$ and $CH_3CH_2(SO_2)OH$ which can be seen at the end of the species tree. As for the catalysts, sulfur released during the reaction and adsorbed by the catalysts can depress the rate of formation of R134a[63]. Other impurities, e.g. arsenic and silica are also found in the feedstock. These are not investigated because of the lack of group contribution data.

Reactions with other impurities in the tri feedstock provide species having similar structures to those appeared in diagram 5.12. This is because most of the impurities found in the feedstock were also generated by the program. Some species with bromine substitution can be found as a result of reactions with bromochloromethane. Reactions with these impurities will not be discussed in detail since the principles of the reactions are similar to that of the main reaction.

5.3.9   Summary

A considerable number of components have been generated by the program, these include those already identified in the existing plant such as carbon tetrachloride, vinyl chloride, ethylene dichloride, 1,1,2-trichloroethane, 1,1,1-trichloroethane, carbon tetrachloride, vinylidene chloride and chloroform. The route generated by the program is different from that of the real process. The process requires a fluorinating agent to convert $-CH_2Cl$ to $-CH_2F$ because it is a difficult conversion, while this program generates species solely based on the criteria of free energy change of reactions.

Components generated in the reactor will be purified from unreacted feed and other byproducts. HF/R133a recycle contains a significant amount of 'heavies' and therefore should be purified to avoid further reactions in the reaction system. During product purification, the feed stream which is the outlet of the first column contains mostly 'light' components. A small number of 'heavies' is recycled into the first column and suspected to accumulate here. However, they could be removed during crude workup. The 'light' stream containing volatile material will be released, and therefore their accumulation is not expected. The product stream contains other material which cannot be removed due to the formation of minimum boiling point and heterogeneous azeotrope between fluorinated and chlorinated compounds.

The running of the program with the presence of impurities has generated an insignificant number of species. Less than a few sulfuric compounds were found, while reactions with arsenic and silica cannot be determined due to lack of group contribution data. Reactions with other impurities produced components with similar types to those of the reactions of the main raw material.
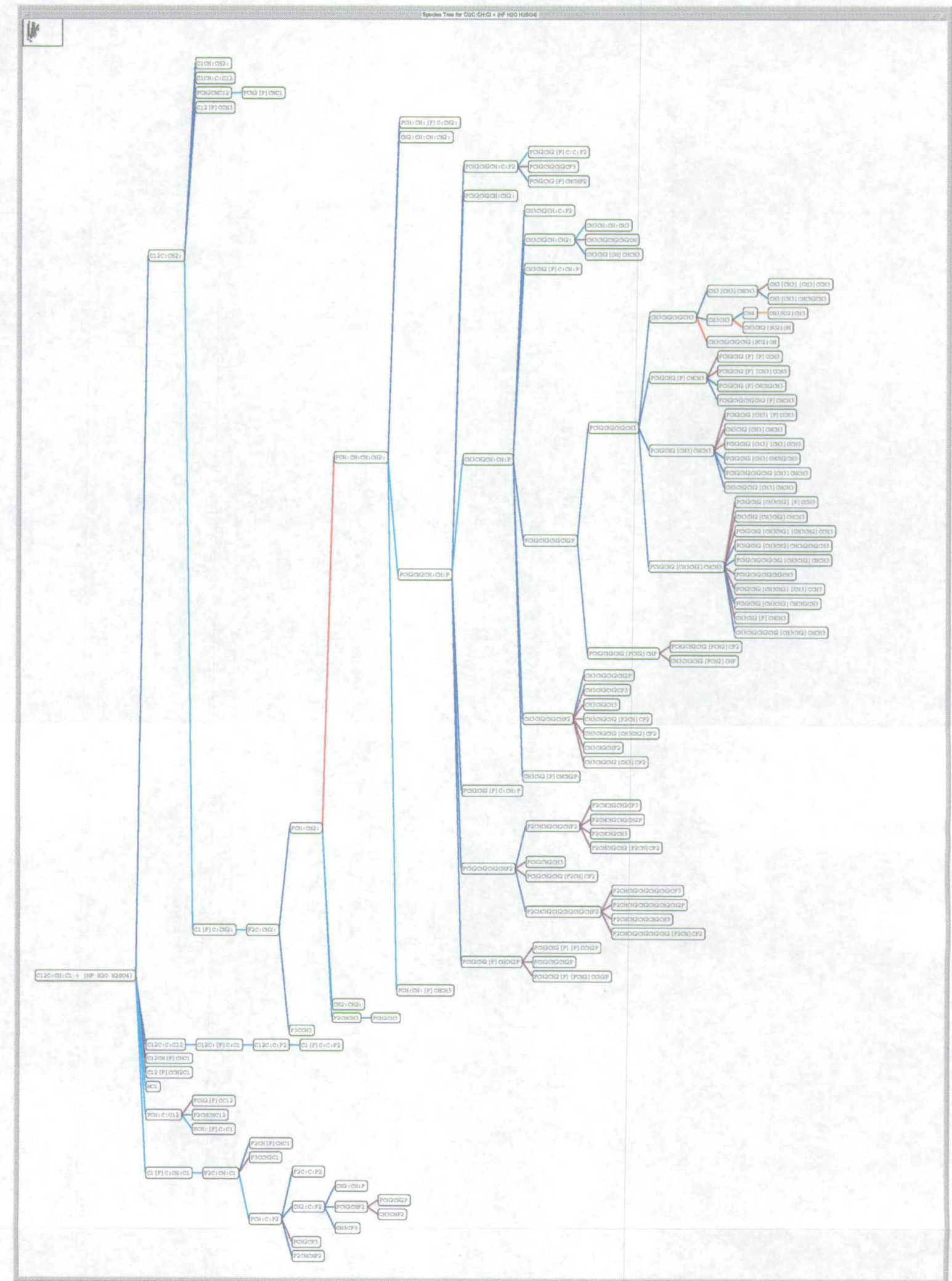
Figure 5.17: The effect of impurities in the R134a reactor

5.4   The R22 Process

The application of automated generation of chemical species and chemical reactions on the preparation process of R-22 (Chlorodifluoromethane) is described in this section. The species generated mainly consisted of chlorinated and fluorinated compounds.

5.4.1   Reaction Analysis

Process Chemistry

R-22 (chlorodifluoromethane; $CHClF_2$) is manufactured by reacting chloroform ($CHCl_3$) with hydrogen fluoride (HF). The main reactions are :

1. $CHCl_3 + HF \rightarrow CHCl_2F + HCl$

2. $CHCl_2F + HF \rightarrow CHClF_2 + HCl$

3. $CHClF_2 + HF \rightarrow CHF_3 + HCl$

$CHCl_2F$ is also called R-21 and CHF_3 is called R-23. The process block diagram can be seen in Figure 5.18.
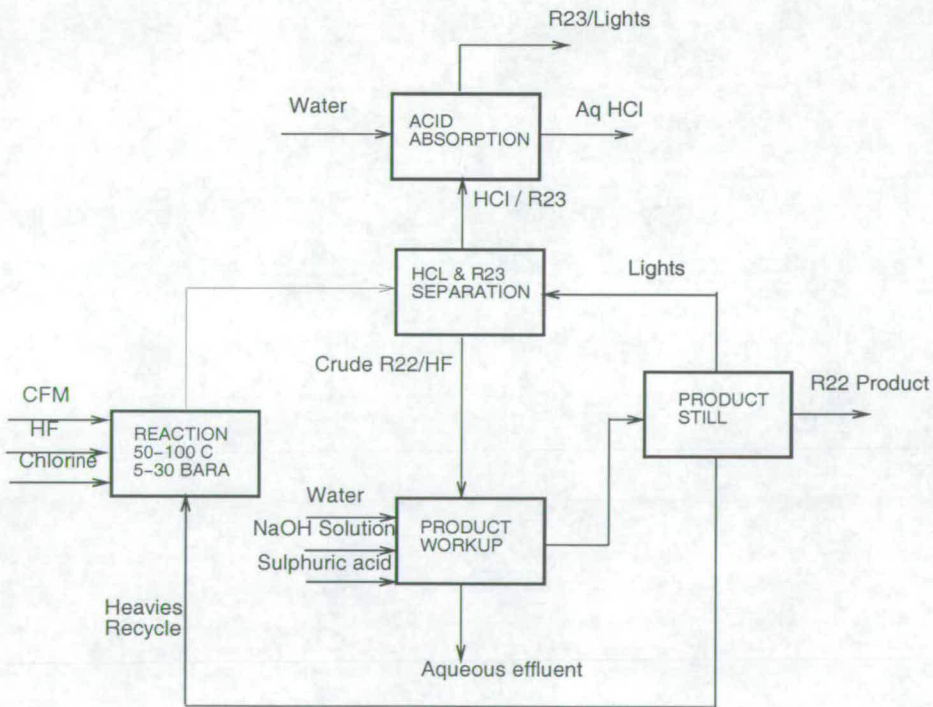
Figure 5.18: R22 Process Flow

Chemistry Principles

These are similar to R-134a synthesis, the production of R-22 involves substitution of halogen, hydrolysis and elimination. Hydrolysis involves the attachment of OH group into the structure.

5.4.2 Results and Analysis

The initial species consist of chloroform (CFM) and anhydrous hydrogen fluoride (HF). The HF feedstock also contains impurities as found in R-134a. CFM contains carbon tetrachloride, methylene chloride, chlorobromomethane, ethylenedichloride, 1,1-dichloroethane, vinylidene chloride and water. The reaction system has 50 - 100 °C operating temperature and 5-30 bar operating pressure. The initial reaction which is considered as **Level 1** produces 6 surviving species generated by the following addition and substitution reactions. The reactions developed by the program at **Level 1** are shown below :

1. $2CHCl_3 \rightarrow CCl_4 + CH_2Cl_2$
   $\Delta G_{298K} = 7.72(kJ/mol)$

2. $2CHCl_3 \rightarrow Cl_2CHCCl_3 + HCl$
   $\Delta G_{298K} = -27.24(kJ/mol)$

3. $CHCl_3 + HF \rightarrow FCHCl_2 + HCl$
   $\Delta G_{298K} = -4.81(kJ/mol)$

The reactions generate the following surviving species : CCl_4, CH_2Cl_2, Cl_2CHCCl_3, HCl, $FCHCl_2$.

The tree diagram of the species formation is presented in Figure 5.19.

It appears that the production of chlorodifluoromethane follows one reaction route, i.e. reaction 3. The reaction path is similar to that of the plant chemistry. In **Level 2**, further substitution of a chlorine atom occurs producing the following reactions and species :

1. $FCHCl_2 + HF \rightarrow HCl + F_2CHCl$
   $\Delta G_{298K} = -4.81(kJ/mol)$

Level 3 involves the reaction of F_2CHCl with HF producing :

1. $F_2CHCl + HF \rightarrow HCl + F_3CH$
   $\Delta G_{298K} = -4.81(kJ/mol)$
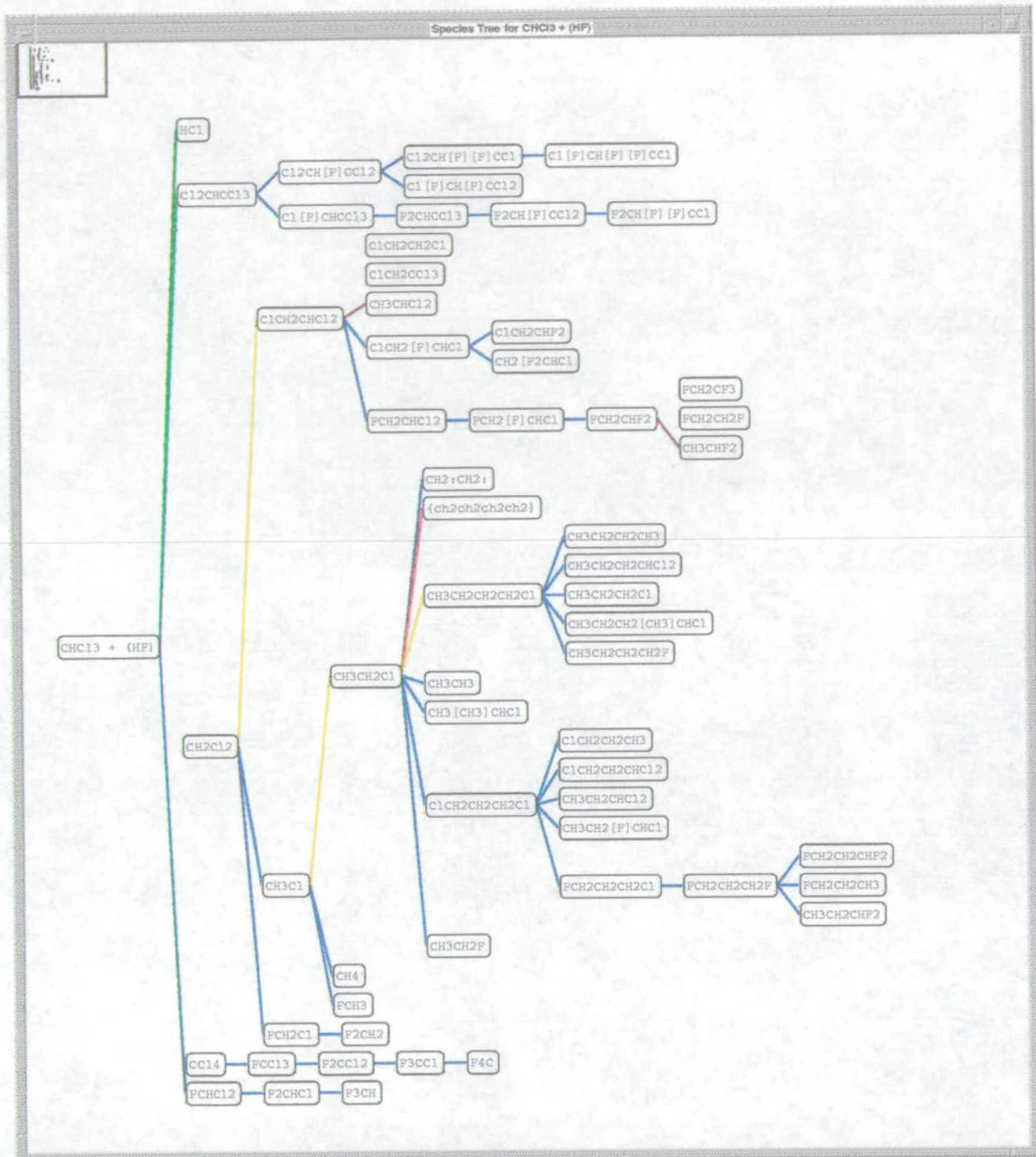
Figure 5.19: The tree diagram of species formation in R-22 Preparation

5.4.3   List of byproducts

In addition to those impurities known to be found in the process, such as methylene chloride, ethylene dichloride and carbon tetrachloride, a number of other species have been generated by the program. Most of these species are chlorinated and fluorinated. The following table presents some of the species generated by the program.

Table 5.11: List of species generated by the program

CCl_4	CH_2Cl_2	Cl_2CHCCl_3
HCl	F_2CHOH	$ClCH_2CCl_34$
CH_3Cl	$ClCH_2CHCl_2$	FCH_2Cl
$ClCH_2CH_2Cl$	CH_3CHCl_2	FCH_2CHCl_2
$FCH_2[F]CHCl$	FCH_2CHF_2	FCH_2CF_3
FCH_2CH_2F	CH_3CHF_2	CH_3CF_3
F_2CHCCl_3	Cl_2CHF_2Cl	$F_2CH[F]CL_2$
CH_3CH_2Cl	$CH_2=CH_2$	$CH_2=CHCl$
C_4H_8	FCH_2CH_2Cl	$FCH_2CH_2CH_3$

The boiling point of R-22 is -40.8 °C (246.7 K). Most chlorinated products have high boiling points, therefore they are not included in the list, while most fluorinated products have low boiling points which are closer to the key component.

5.4.4 R-22 Purification

R-22 purification process comprises several stages : reaction still, HCl and R23 removal, crude workup and product distillation. Reaction still is used to remove unreacted CFM, R21 from the main off gas, but it is not included in this study. Before entering crude workup, HCl and R23 are separated first, and the crude containing R22 is washed by water, NaOH solution and sulphuric acid. Pure R22 is taken from the product of the distillation column, while light components are taken overhead and recycled into the HCl-R23 separation column. The heavy components are recycled into the reactor.

The flow of the separation simulation can be seen in Figure 5.20 and the results are presented in Table 5.13.

5.4.5 Relative Volatility

Table 5.12: List of species generated by the program

Component	Relative volatility
$CH_2=CH_2$	15.08300
HCl	10.30429
CHF_3	9.148437
CH_3CH_3	8.103450
$CHClF_2$	1.000000
CH_3CH_2F	0.8589062
CH_3Cl	0.4386867
$CH_2=CHCl$	0.2645108
$CHCl_2F$	7.989402E-02
HF	4.209770E-02
CH_2Cl_2	1.355335E-02
$CHCl_3$	4.302370E-03
CCl_4	2.338226E-03
$ClCH_2CH_2Cl$	1.140252E-03
H_2O	2.449973E-04
$ClCH_2CHCl_2$	2.085806E-04
Cl_3CCHCl_2	7.730277E-06

5.4.6 RADFRAC Simulation
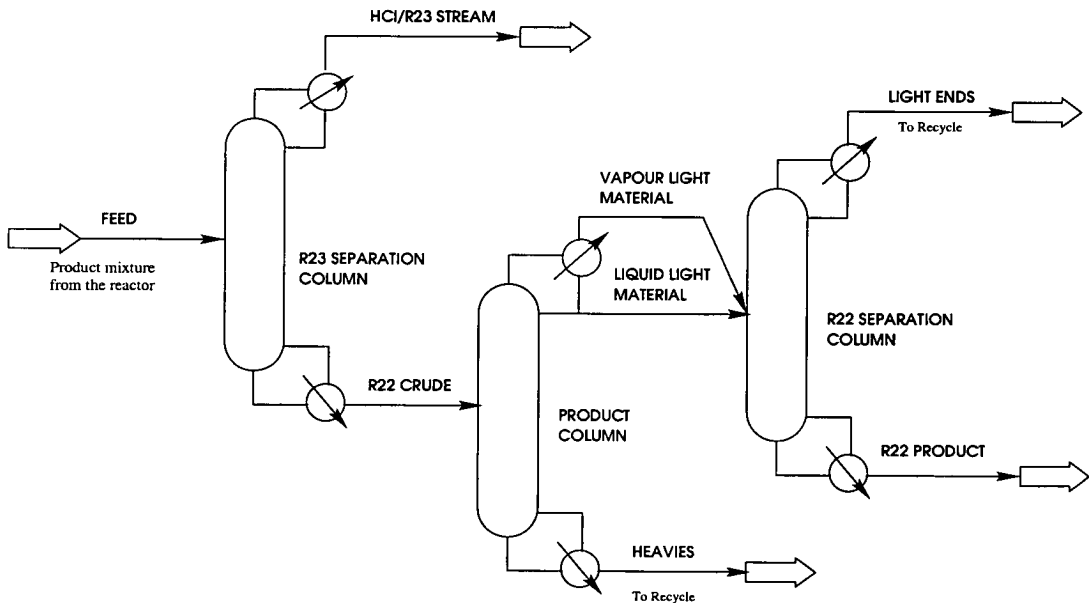
Figure 5.20: R-22 Purification Simulation

17 components have been selected for the purpose of separation simulation. Some of these components have close boiling points to the key component, i.e. CH_3CH_3. The results show that, sharp separation occurs providing relatively clean split between the 'lights' and the 'heavies' in the three separation columns. Trace amount of light components appear in the bottom product, and likewise for the heavy components in the top product.

The study on side reaction generation of R-22 process indicates the generation of chlorinated and fluorinated components which can be categorized in class IV and II respectively. The presence of these two classes together forms limited solubility, indicates that the magnitude in deviation of Raoult's law is relatively limited. This results in the formation of minimum boiling and heterogeneous azeotropes. The present of water in the raw material may propagate hydrolysis reaction producing components containing OH group, however, such components do not prevail since the addition of OH group requires large free energy change. Therefore, the maximum boiling azeotrope mixture is unlikely to form and undesired components seem to be separable from the main product. Material accumulation in the process line cannot be minimized or avoided, since the 'heavies' and the 'lights' are recycled back to the process line. Both recycles contain materials which cannot be removed during product workup of HCl/R23 separation.

Table 5.13: Results of simulation, component flow in kmol/hr

Streams	Feed	HCL-R23 Stream	R22 CRUDE	VAP-LIGHT MATERIAL	LIQ-LIGHT MATERIAL	HEAVIES	LIGHT ENDS	R22 PRODUCT
From Unit		R23-SEP	R23-SEP	PRO COL	PRO COL	PRO COL	R22-SEP	R22-SEP
To Unit	R23-SEP		PRO COL	R22-SEP	R22-SEP			
Temperature, $^\circ$ C	20.0	-82.8	-41.4	-42.8	-42.8	37.3	-45.2	-41.4
Mole flow, kmol/hr	26.5	5.0	21.5	1.025	19.475	1.0	1.5	19.0
$CH_2{=}CH_2$	0.1	0.99	0.001	< 0.001	< 0.001	trace	0.001	trace
HCl	0.1	0.097	0.003	0.001	0.002	trace	0.003	trace
CHF_3	5.0	4.710	0.290	0.088	0.203	trace	0.290	trace
CH_3CH_3	0.1	0.094	0.006	0.002	0.005	trace	0.006	trace
$CHClF_2$	20.0	trace	20.0	0.928	19.027	trace	1.199	18.801
CH_3CH_2F	0.1	trace	0.1	0.004	0.096	trace	0.001	0.099
CH_3Cl	0.1	trace	0.1	0.002	0.098	< 0.001	trace	0.1
$CH_2{=}CHCl$	0.1	trace	0.1	trace	< 0.001	0.1	trace	< 0.001
$CHCl_2F$	0.1	trace	0.1	trace	trace	0.1	trace	trace
HF	0.1	trace	0.1	trace	trace	0.1		
CH_2Cl_2	0.1	trace	0.1	trace	trace	0.1		
$CHCl_3$	0.1	trace	0.1	trace	trace	0.1		
CCl_4	0.1	trace	0.1	trace	trace	0.1		
$ClCH_2CH_2Cl$	0.1	trace	0.1	trace	trace	0.1		
H_2O	0.1	trace	0.1	trace	trace	0.1		
$ClCH_2CHCl_2$	0.1	trace	0.1	trace	trace	0.1		
Cl_3CCHCl_2	0.1	trace	0.1	trace	trace	0.1		

5.4.7 Assessment of Compounds Carried Over in the Recycle Streams

Feed stream from the reactor effluent entering the separation process contains main product R22 (chlorodifluoromethane) as well as other byproducts such as hydrogen chloride, ethylene, ethane, trifluoromethane, dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, water and so on. In the first column, HCl and R23 (trifluoromethane), which is found in a considerable amount as a major byproduct, and other 'light' components, are separated first. The bottom stream contains R22 and the 'heavies' and also some of the 'light' components which cannot be removed. Most of the 'heavies' are chlorinated compounds. In the second column where R22 purification is held, the 'heavies' containing components such as vinyl chloride, dichloromethane, chloroform and 1,1,2-trichloroethane can be completely separated and recycled into the reactor. The recycle of these components into the reactor can cause further reactions. Therefore, the crude workup which is available before the second column may be useful to remove most of these components. The crude treatment will reduce the separation and the reactor load. Further reactions of the 'heavy' components might produce deposit and contaminate the catalyst in the reactor.

In the third column, where R22 is taken as product in the bottom stream, the 'light' components can be removed almost completely results in a very high product purity. However the overhead stream containing ethylene, ethane, trifluoromethane and the other 'lights' is recycled back into the first separation column. If non-sharp separation occurs in the HCl/R23 separation column, then these components will accumulate in the process stream and occasional purge will be needed.

C2H4	0.00067	HF	0.0
HCl	0.0020	CH2Cl2	0.0
CHF3	0.1933	CHCl3	0.0
C2H6	0.0040	CCl4	0.0
CHClF2	0.7993	C2H4Cl2	0.0
C2H5F	0.00067	H2O	0.0
CH3Cl	0.0	C2H3Cl3	0.0
C2H3Cl	0.0	C2HCl5	0.0
CHCl2F	0.0		

C2H4	0.0198	HF	0.0
HCl	0.0194	CH2Cl2	0.0
CHF3	0.942	CHCl3	0.0
C2H6	0.0188	CCl4	0.0
CHClF2	0.0	C2H4Cl2	0.0
C2H5F	0.0	H2O	0.0
CH3Cl	0.0	C2H3Cl3	0.0
C2H3Cl	0.0	C2HCl5	0.0
CHCl2F	0.0		

	VAP LIGHT / LIQ LIGHT		VAP LIGHT / LIQ LIGHT
C2H4	0.0 / 0.0	HF	0.0 / 0.0
HCl	0.00097 / 0.0001	CH2Cl2	0.0 / 0.0
CHF3	0.08585 / 0.0104	CHCl3	0.0 / 0.0
C2H6	0.00195 / 0.00026	CCl4	0.0 / 0.0
CHClF2	0.90537 / 0.97931	C2H4Cl2	0.0 / 0.0
C2H5F	0.0039 / 0.00493	H2O	0.0 / 0.0
CH3Cl	0.00195 / 0.00503	C2H3Cl3	0.0 / 0.0
C2H3Cl	0.0 / 0.0	C2HCl5	0.0 / 0.0
CHCl2F	0.0 / 0.0		

HCL / R23

LIGHT COMPONENTS TO RECYCLE

R22 PURIFICATION COLUMN-2

C2H4	0.00377
HCl	0.00377
CHF3	0.18868
C2H6	0.00377
CHClF2	0.75472
C2H5F	0.00377
CH3Cl	0.00377
C2H3Cl	0.00377
CHCl2F	0.00377
HF	0.00377
CH2Cl2	0.00377
CHCl3	0.00377
CCl4	0.00377
C2H4Cl2	0.00377
H2O	0.00377
C2H3Cl3	0.00377
C2HCl5	0.00377

FEED

HCL / R23 SEPARATION COLUMN

R22 CRUDE

VAPOUR LIGHT MATERIAL

LIQUID LIGHT MATERIAL

R22 PRODUCT

C2H4	0.0	HF	0.0
HCl	0.0	CH2Cl2	0.0
CHF3	0.0	CHCl3	0.0
C2H6	0.0	CCl4	0.0
CHClF2	0.9895	C2H4Cl2	0.0
C2H5F	0.0052	H2O	0.0
CH3Cl	0.00526	C2H3Cl3	0.0
C2H3Cl	0.0	C2HCl5	0.0
CHCl2F	0.0		

R22 PURIFICATION COLUM-1

C2H4	0.00005	HF	0.00465
HCl	0.00014	CH2Cl2	0.00465
CHF3	0.01349	CHCl3	0.00465
C2H6	0.00028	CCl4	0.00465
CHClF2	0.93023	C2H4Cl2	0.00465
C2H5F	0.00465	H2O	0.00465
CH3Cl	0.00465	C2H3Cl3	0.00465
C2H3Cl	0.00465	C2HCl5	0.00465
CHCl2F	0.00465		

HEAVIES TO RECYCLE

C2H4	0.0	HF	0.1
HCl	0.0	CH2Cl2	0.1
CHF3	0.0	CHCl3	0.1
C2H6	0.0	CCl4	0.1
CHClF2	0.0	C2H4Cl2	0.1
C2H5F	0.0	H2O	0.1
CH3Cl	0.0	C2H3Cl3	0.1
C2H3Cl	0.1	C2HCl5	0.1
CHCl2F	0.1		

NOMENCLATURE

C2H4	ETHYLENE
HCl	HYDROGEN CHLORIDE
CHF3	TRIFLUOROMETHANE
C2H6	ETHANE
CHClF2	CHLORODIFLUOROMETHANE
C2H5F	ETHYL-FLUORIDE
CH3Cl	METHYL-CHLORIDE
C2H3Cl	VINYL-CHLORIDE
CHCl2F	DICHLOROMONOFLUOROMETHANE
HF	HYDROGEN-FLUORIDE
CH2Cl2	DICHLOROMETHANE
CHCl3	CHLOROFORM
CCl4	CARBON-TETRACHLORIDE
C2H4Cl2	1,2-DICHLOROETHANE
H2O	WATER
C2H3Cl3	1,1,2-TRICHLOROETHANE
C2HCl5	PENTACHLOROETHANE

Figure 5.21: Fractions of components in the process flows after R22 Purification

5.4.8 The Effect of Impurities in the Feedstock

Similar to the R134a process, the feedstock of the R22 process contains sulfuric acid, AsF_3, AsF_5, and H_2SiF_6. The study on the reaction of sulfuric acid with other compounds is presented in the following two species tree diagrams (Figures 5.22 and 5.23). Since alkanes are capable of reacting with sulfuric radicals, then the reaction of ethane which is generated in the first diagram is run in the second diagram. The results are similar to the R134a where reactions with H_2SO_4 seems difficult to achieve. The components that can be generated are: $CH_3(SO_2)OH$, $CH_3CH_2(SO_2)OH$, $CH_3CH_2CH_2(SO_2)OH$ and some longer chains whenever alkanes are generated.

Some of the impurities found in the CFM feedstock were generated by the program and can be seen in Figure 5.19. The impurities such as carbon tetrachloride, methylene chloride and ethylenedichloride were generated by the program. Reactions with these compounds led to the formation of longer chain, or other chlorinated and fluorinated components. Bromine addition to some species were obtained as a result of reactions with bromochloromethane. Reactions of these impurities will not be discussed in detail, since the principles of the reactions are similar to that of the main reaction.

5.4.9 Results of the Program Run Times

Similar to the case study in the previous chapter, the program was run on SUN SPARC Ultra Machine using UNIX Solaris 2.6 operating system. The duration to process oxychlorination reactions, direct chlorination, pyrolysis, R134a and R22 was about 40-60 minutes due to a relatively smaller number of new species generated. To run multi component input as the initial reactants as in Figure 5.16 required 2 days (about 50 hours) to complete. This suggests that running combinatorial problem in this method consumes large computing resources.

5.4.10 Summary

The application of the program in the synthesis of R-22 has produced a favourable result. The program is able to generate all components found in the real process, including carbon tetrachloride, methylene chloride, chlorobromomethane, ethylene dichloride, 1,1-dichloroethane, vinylidene chloride and water. High purity product can be obtained from the separation process, but a number of 'light' components can accumulate in the process line due to non-sharp split during HCl/R23 separation. 'Heavy' components from the product separation column might accumulate if the recycle is continuously fed into the reactor. Further reactions of these components could cause deposit problem and generate longer chains. Therefore, crude workup and ventilation are needed to remove these 'undesired' components and reduce the load of the reactor and the separation units.

By running the program with more species and more cycles, the number of possibilities increased quite considerably. The effect can be seen in Figure 5.23. Coupling of species may occur and produce new components with longer carbon chain. Reaction with impurities such as H_2SO_4 seems difficult to achieve. Therefore, there is only a small

amount of sulfuric components generated. Reactions of other impurities present in CFM feedstock produce components which have similar types to those of the species generated from the reactions of the main raw material.
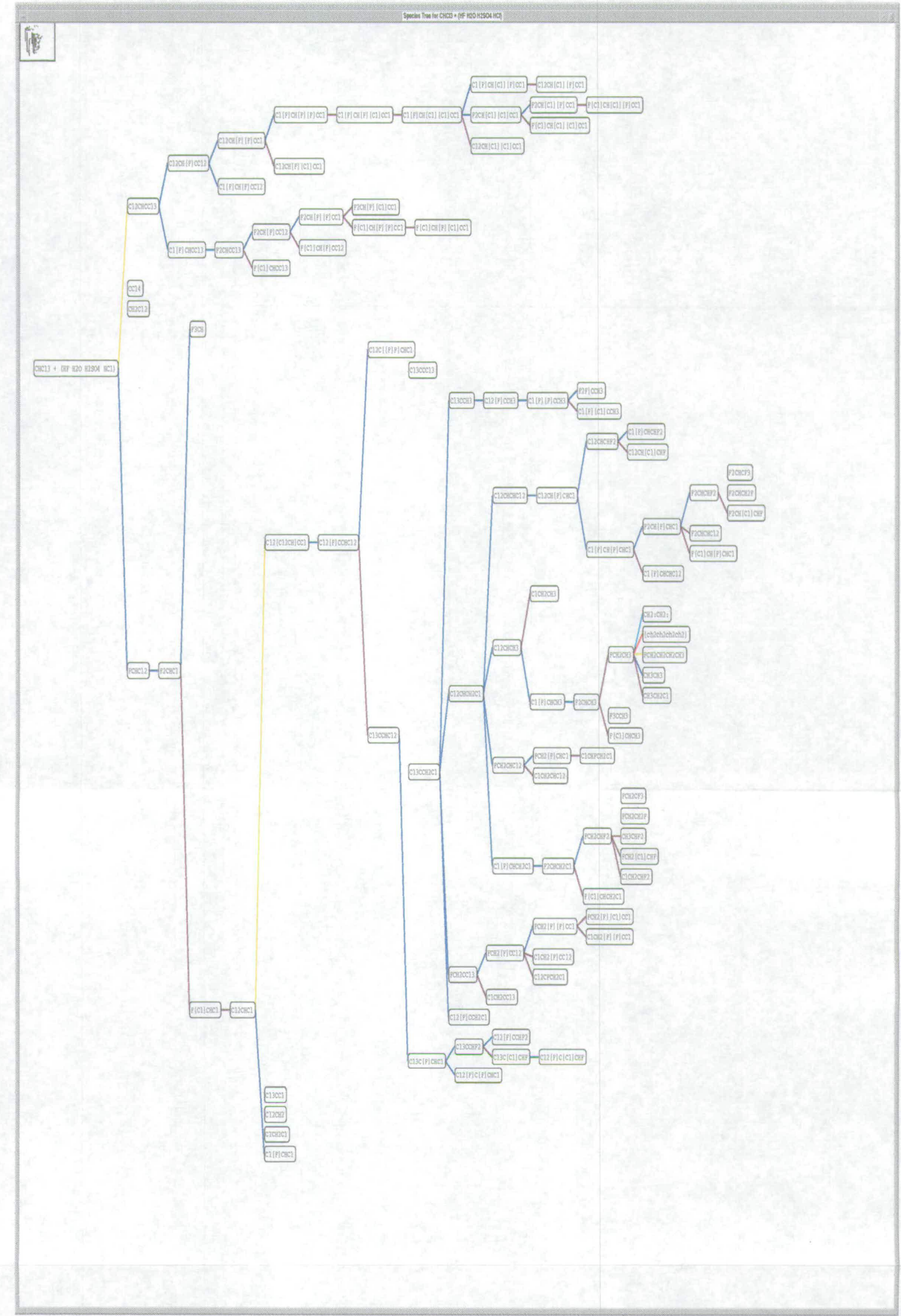
Figure 5.22: The effect of impurities in the R22 reactor (a)
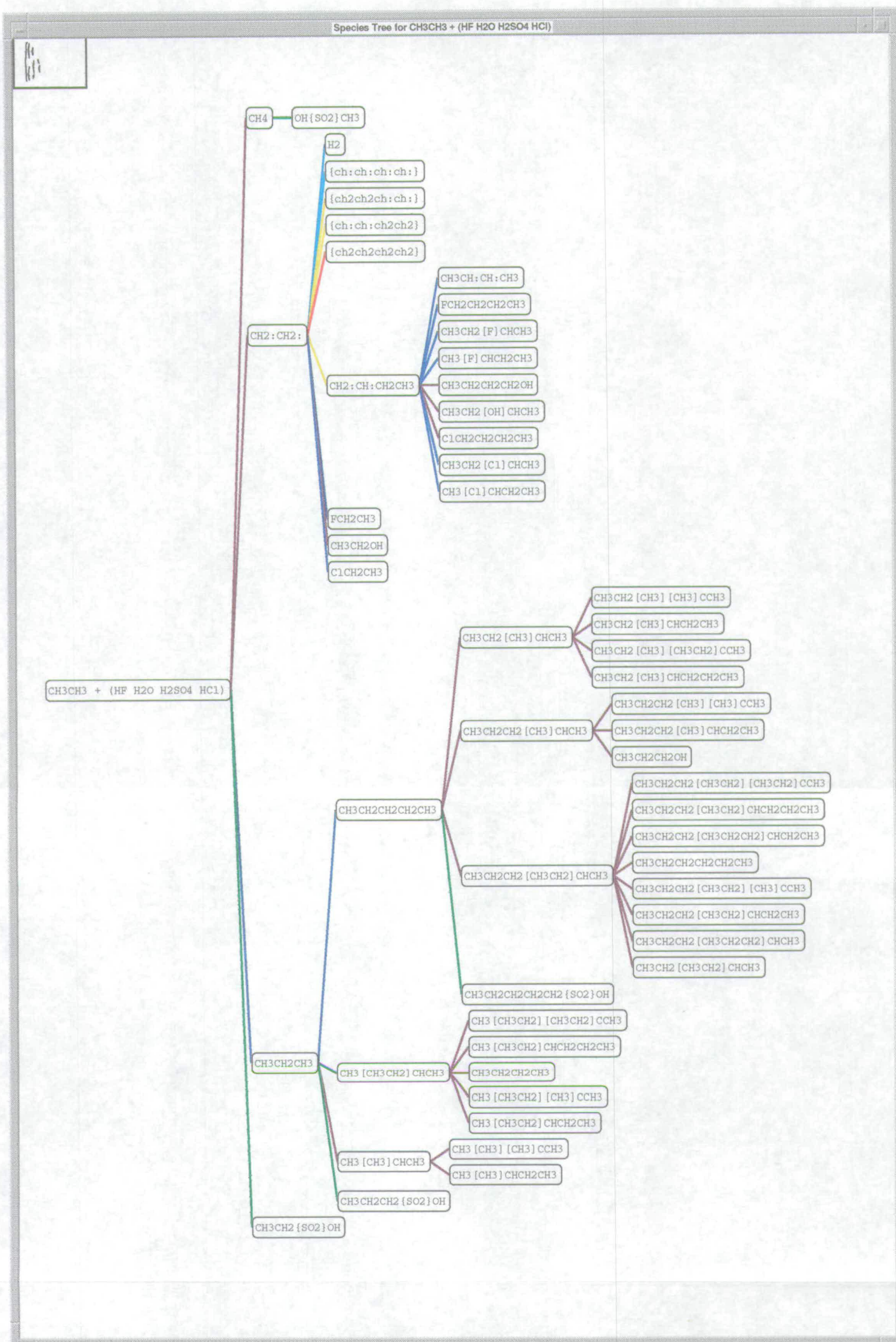
Figure 5.23: The effect of impurities in the R22 reactor (b)

Chapter 6

Conclusions and Recommendations

6.1 Conclusions

6.1.1 Literature Review

Previous work in the synthesis of reaction paths can be divided in two areas :

- Reaction Path Synthesis
  This area focused on developing methods to construct reaction pathways. The methods were based on qualitative approaches and were heuristic in nature, using the concepts of stoichiometric and thermodynamic constraints. The application of these methods to several known 'reaction clusters' showed that the approach was able to find a number of feasible reactions to replace the net infeasible reaction. However, these methods could not be automated. This approach did not seem to be suitable for our purpose of generating large number of side reactions.

- Automated Reaction Path Synthesis
  Several efforts had been made to couple the use of computers, chemical structure representation and reaction path generation. The application of this earlier work was limited to storing and retrieving information from databases. Recent development on automated generation of reaction paths was the construction of languages for chemical reactions, namely Language for Chemical Reactions (LCR) and Reaction Description Language (RDL). The languages were established from the concept of fundamental chemistry. The comprehensive approach of the real chemistry enabled the methods to generate reaction networks and model complex reaction systems. For molecular representation, RDL used line notations which required further interpretation to obtain the meaning of the notation, while LCR used object oriented programming. For the purpose of our work, these approaches were too detailed and the implementation required complex programming structures.

6.1.2 Representation of Structures

Since the work in this thesis is aimed at identifying side reactions and all possible byproducts that can be generated, representation of chemical structures is crucial. We applied functional groups as in group contribution technique for property estimation, where the chemical structures were constructed from the functional groups. The use of functional group technique has been found useful and enables the structures to be represented and manipulated conveniently. The chemical structures constructed from functional groups are unambiguous and carry all necessary information. In determining radical formation, bond fragmentation can be carried out directly from these structures. Furthermore, chemical properties can also be determined directly from the group property method.

6.1.3 Preliminary studies of known reactions

These studies were conducted to establish the relation of thermodynamic requirements of the existing chemical reactions. Hence, a condition of plausibility was formulated and used as a platform to determine feasible reactions. The condition of plausibility was used for all applications in this work.

From three common industrial reactions, namely chlorination of methane, HDA and HCN manufacture, we could identify :

1. Reactions that should definitely take place have negative free energy.

2. Reactions that are not likely to occur have positive free energy.

3. Reactions that are known to occur, but have positive free energy. This fact is acceptable from industrial point of view, where feasible reactions may undergo at slightly positive free energy, i.e. 40 kJ/mol[6].

4. Reactions that are not known to occur but have negative free energy. The reactions might be the summation of several reactions which have negative free energy.

Based on categories 1-3, we justified the condition of plausibility, where free energies were calculated within two conditions :

- Relaxed constraints on free energies. Free energies were estimated at maximum $\Delta G = 40$ kJ/mol under specified reaction conditions.

- Relaxed temperature range. Temperatures were considered within the range of 298 K up to 1500 K, while free energies were maintained at negative values.

Reactions which satisfy the above conditions were considered feasible.

6.1.4 Comparisons with experiments

We applied the programs to experimental studies of partial wet oxidation of p-coumaric acid and alkylation of toluene with ethanol. The results generated by the programs were compared to those generated by the experiments. It was found that all components identified in the experiments could be generated by the programs. Beside that, the programs also generated components which were not detected in the experiments. This might be because of several factors :

- Such components were present in minute quantities, and thus were not detected.

- The program generated reaction routes which were not found in the experiments. It was suspected that thermodynamic selectivity plays its role here. Reactions compete through the values of free energy. The selectivity of a reaction is toward more negative free energy. Therefore, a reaction which is theoretically feasible, may not be found in reality.

- The use of catalysts in the experiments may provide different results. By changing rates dramatically, catalysts could apparently suppress the formation of certain components, so they were found in the experiments.

Sensitivity analysis was conducted to investigate the number of species generation in relation with the value of free energy and temperature. This was done on the oxidation reaction of p-coumaric acid. We found that there was a threshold value associated with free energy to determine process feasibility. Slightly different networks have been obtained as a result of applying four different values of free energy as the tuning parameter, i.e. strictly negative, maximum 10 kJ/mol, maximum 40 kJ/mol and negative but having a wider temperature bound (298 - 1500 K). The sensitivity study showed that small positive free energy, i.e. 10 kJ/mol under moderate condition, appears to be sensible for feasibility evaluation. The network generated was the most closely resembled the experimental results. This can be also be justified on the examination of the accuracy of Joback group contribution technique, where the difference between the literature data and the estimation is 20-30 kJ/mol. The application of 10 kJ/mol is within this range of error.

6.1.5 Studies on Side Reaction Generation in Identified Processes

The studies were performed on three industrial processes :

1. The vinyl chloride monomer process

2. The R134 process

3. The R22 process

In these studies, the free energy of 10 kJ/mol was applied to estimate feasible reactions. Separation simulation was conducted using the ASPEN package.

The results showed that a considerable number of byproducts may be generated in all three processes. In the VCM process, both chlorinated and oxygenated compounds were generated in the oxychlorination reactors. Some of these components have close boiling points to the key components. The closeness of the boiling points was a determining factor in the separability of the components. Both aspects, the type of components and the boiling points, caused azeotrope formation. This was shown by the simulation studies where sharp separation and thus high purity product were difficult to achieve. Other components which could be separated, such as the 'heavies' and the 'lights', were recycled into the reactors and separation systems and remain in the process.

In the R134 and R22 processes, components generated were mostly chlorinated and fluorinated. These could form minimum boiling point and heterogeneous azeotropes. However, relatively sharp separation is possible and small amounts of undesired species appear in the product stream. Other components that could be separated were recycled back into the reactor and some light components could be removed by incineration.

In the studies of R134 and R22 processes, the effect of impurities was also investigated. It has been found that impurities carried in the feedstock could react and generate more species. Most of these impurities were also generated by the program from the reactions of the inital main raw materials.

These studies confirmed that many potential byproducts would be difficult to separate and tend to accumulate in the recycle streams. This also indicated the necessary implementation of crude workup to remove some of the components, such as chemical washing to get rid of oxygenated and heavily chlorinated components before the separation process.

The results of the application of this work showed that the approach has a promise for identifying possible side reactions, byproducts and the problems what they might cause in a continuous process. Thus in the long term the approach might be about the possibility of reducing and eliminating pilot plant studies in moving from laboratories to full scale processes.

6.1.6 Computing Run Times

There is a variation in the computing run times to process the reactions in the case studies. The duration is according to the number of the initial species, the number of nodes to be expanded and the number of products to be considered. The larger the number of the initial species as the input, it is more likely that the larger the number of possible products. Hence, it takes longer to accomplish the task. The variation in the processing time ranges from 10 minutes to several days. The significant impact on the variation of the run times is caused by the program for reaction generation.

6.2   Recommendations and Future Work

We have shown that the programs can be used in various applications such as comparisons with experiments and assessment of byproduct generation in industrial processes. The method suggested here has the potential for wider applications.

However, the performance of the programs needs to be improved. The combinatorial approach used in reaction generation is a drawback since it consumes large computing resources. The number of possibilities increases significantly if the number of components to be investigated is more than five. It would be desirable to improve the performance by applying a mathematical approach. The use of integer programming for solving large complex problem in process synthesis as shown in other synthesis problems such as heat exchanger network and multicomponent distillation separation, could reduce the size of the searching problem quite considerably.

It would be very desirable to enlarge the group database to handle components with fused rings and enable the programs to run more complicated structures such as that of enzymes, pharmaceuticals and carbohydrates. It is highly desirable to improve the accuracy of the property estimation method. For some compounds, the accuracy of Joback group contribution methods are uncertain, so other methods such as Benson[64, 65], Gani[66, 67] or quantum chemistry[68, 69] needs to be considered. Benson's method provides more detailed representation of groups, so errors can be reduced. Gani used molecular structure based property estimation to predict the activities. Quantum chemistry provides calculation using electron configuration interactions, therefore it is expected to be more accurate, although currently the computational requirements are very large.

Bibliography

[1] Siirola, J.J., (1995), *An Industrial Perspective on Process Synthesis*, AIChE Symp. Series, 91, 222-233.

[2] Douglas, J.M. and Stephanopoulos, G., (1995) *Hierarchical Approach in Conceptual Process Design: Framework and Computer-Aided Implementations*, AIChE Symp. Series, 91, 183-197.

[3] Nishida, N., Stephanopoulus, G. and Westerberg, A. W., (1981), *A Review of Process Synthesis*, AIChE Journal, **27**, 3, 321-351.

[4] Flower, J. R., Bikos, S.C. and Johnson, S.W., (1995), *A Modular Approach to Synthesis of Cleaner Processes*, Comp. Chem. Engng., 19, Suppl., S45-S50.

[5] Douglas, J.M., (1988), *Conceptual Design of Chemical Processes*, Mc Graw Hill International Editions, New York, 99-103.

[6] May, D. and Rudd, D.F., (1976), *Development of Solvay Clusters of Chemical Reactions*, Chem. Eng. Sci., 31, 59 - 69.

[7] Rudd, D.F. (1976), *Accessible Designs in Solvay Cluster Synthesis*, Chem. Eng. Sci., 31, 701-703.

[8] Lowenheim, F.A. and Moran, M.K., (1975), *Faith, Keyes and Clark's Industrial Chemicals*, 4th ed., John Wiley & Sons, New York, 795, 230, 345, 496, 109, 487, 397, 164, 1, 482, 769, 244, 862.

[9] Rotstein, E., Resasco, D. and Stephanopoulos, G., (1982), *Studies on the Synthesis of Chemical Reaction Paths-I : Reaction Characteristics in the $(\Delta G, T)$ Space and A Primitive Synthesis Procedure*, Chem. Eng. Sci., **37**, 9, 1337-1352.

[10] Fornari, T. and Stephanopoulos, G., (1994), *Synthesis of Chemical Reaction Paths: Economic and Specification Constraints*, Chem. Eng. Comm., 129, 159-182.

[11] Buxton A., Livingston, A.G. and Pistikopoulos, E.N., (1997), *Reaction Path Synthesis for Environmental Impact Minimization*, presented at Workshop on Process Systems Engineering, York.

[12] Pistikopoulos,E.N., Stefanis,S.K. and Livingston,A.G., (1994), *A Methodology for Minimum Environmental Impact Analysis*, AIChE Symposium Series, **90**, 303,139-150.

[13] Stefanis, S.K., Buxton, A., Livingston, A.G. and Pistikopoulos, E.N., (1996), *A Methodology for Environmental Impact Minimization: Solvent Design And Reaction Path Synthesis Issues*, Comp. Chem. Engng., 20, Suppl., S1419-S1424.

[14] Mavrovouniotis, M.L., (1995), *Symbolic And Quantitative Reasoning: Design of Reaction Pathways through Recursive Satisfaction of Constraints*, Advances in Chemical Engineering, 21, 147-186.

[15] Happel, J. and Sellers, P.H., (1982), *Multiple Reaction Mechanisms in Catalysis*, Ind. Eng. Chem. Fundam., 21, 67-76.

[16] Happel, J., Sellers, P.H. and Otarod, M., (1990), *Mechanistic Study of Chemical Reaction Systems*, Ind. Eng. Chem. Res., 29, 1057-1064.

[17] Mavrovouniotis, M. L. and Stephanopoulos, G, (1992), *Synthesis of Reaction Mechanisms Consisting of Reversible and Irreversible Steps. 1. A Synthesis Approach in the Context of Simple Examples*, Ind. Eng. Chem. Res., 31, 1625-1637.

[18] Mavrovouniotis, M. L., (1992), *Synthesis of Reaction Mechanisms Consisting of Reversible and Irreversible Steps. Formalization and Analysis of the Synthesis Algorithm*, Ind. Eng. Chem. Res., 31, 1637-1653.

[19] Mavrovouniotis, M.L., Stephanopoulos, G. and Stephanopoulos, G., (1992), *Synthesis of Biochemical Production Routes*, **16**, 6, 605-619.

[20] Douglas, J. M., (1990), *Synthesis of Multistep Reaction Processes*, Proceedings of 3rd Internation Conference on Foundations of Computer-Aided Process Design, 79-103.

[21] Phimister, J., (1995), *Synthesis and Assessment of Multistep Process Plant Configurations*, MSc Thesis, Dept. of Chemical Engineering, University of Edinburgh, UK.

[22] Phimister, J., Fraga, E.S. and Ponton, J.W., (1999), *The Synthesis of Multistep Process Plant Configurations*, Comp. and Chem. Eng., **23**, 3, 315-327.

[23] Miller, D.C. and Davis, J.F., (1999), *Integration Chemistry Process Development with Downstream Considerations*, Conference paper, FOCAPD '99 : Computer Aided Design for the 21st Century, July 18-23, Colorado, USA.

[24] Nagel, C.J. and Stephanopoulos, G., (1995), *Inductive and Deductive Reasoning: The Case of Identifying Potential Hazards in Chemical Processes*, Advances in Chemical Engineering, 21, 187-255.

[25] Nagel,C.J., Han,C. and Stephanopoulos, G., (1995), *Modeling Languages: Declarative and Imperative Descriptions of Chemical Reactions and Processing Systems*, Advances in Chemical Engineering - Intelligent Systems in Process Engineering. Part I : Paradigms from Product and Process Design, 21, 1-91.

[26] Blair, J., Gasteiger, J., Gillespie, C., Gillespie, P.D. and Ugi, I., (1974), *Representation of the Constitutional and Stereochemical Features of Chemical Systems in the Computer Assisted Design of Syntheses*, Tetrahedron, 30, 1845-1895.

[27] Blair, J., Gasteiger, J., Gillespie, C., Gillespie, P.D. and Ugi, I., (1974), *CICLOPS: A Computer Program for the Design of Syntheses on the Basis of a Mathematical Model*, Computer Representation and Manipulation of Chemical Information, John Wiley & Sons, New York, 1974, 129-145.

[28] Wipke, T., (1974), *Computer-Assisted Three-Dimensional Synthetic Analysis*, Computer Representation and Manipulation of Chemical Information, John Wiley & Sons, New York, 1974, 147-174.

[29] Govind, R. and Powers, G.J., (1981), *Studies in Reaction Path Synthesis*, AIChE Journal, **27**, 3, 429 - 442.

[30] Clymans, P.J. and Froment, G.F., (1984), *Computer Generation of Reaction Paths and Rate Equations in the Thermal Cracking of Normal and Branched Paraffins*, Comp. Chem. Engineering, **8**, 2, 137-142.

[31] Mavrovouniotis, M. L. and Bonvin, D., (1995), *Towards Design of Reaction Paths*, AIChE Symp. Series, 91, 41-51.

[32] Prickett,S.E. and Mavrovouniotis, M.L., (1997), *Construction of Complex Reaction Systems. 2. Molecule Manipulation and Reaction Application Algorithms*, paper to be published.

[33] Prickett,S.E. and Mavrovouniotis, M.L., (1997), *Construction of Complex Reaction Systems - III. An Example: Alkylation of Olefins*, Comp. Chem. Engng., 21, 12, 1325-1337.

[34] Weininger, D., (1988), *SMILES, a Chemical Language and Information System. 1. Introduction to Methodology and Encoding Rules*, J. Chem. Inf. Comput. Sci., 28, 31-36.

[35] Isaac, N.S., (1975), *Reactive Intermediates in Organic Chemistry*, John Wiley & Sons, London, 294-374.

[36] Finar, I.L., (1975), *Organic Chemistry Vol II : Stereochemistry of Natural Products*, 5th edition, Longman, 48-62.

[37] Kyle, B.G., (1992), *Chemical and Process Thermodynamics*, 2nd edition, PTR Prentice Hall, NJ, 336-364.

[38] Denbigh, K.G., (1997) *The Principles of Chemical Equilibrium*, 4th edition, Cambridge University Press, UK, 143-146.

[39] Reid, R.C., Prausnitz, J.M. and Poling, B.E., (1987), *The Properties of Gases & Liquids*, 4ed, Mc Graw Hill Book Co., 14-15.

[40] Reid, R.C., Prausnitz, J.M. and Poling, B.E., (1987), *The Properties of Gases & Liquids*, 4ed, Mc Graw Hill Book Co., 154-156.

[41] Winston,P.H., (1993), *Artificial Intelligence*, 3ed, Addison Wesley Publishing Co., 63-100.

[42] Mantzavinos, D., Hellenbrand, R., Metcalfe, I.S. and Livingstone, A.G., (1996), *Partial Wet Oxidation of p-Coumaric Acid: Oxidation Intermediates, Reaction Pathways and Implications for Wastewater Treatment*, Wat. Res., **30**, 12, 2969-2976.

[43] Herrera, F., Pulgarin, C., Nadtochenko, V. and Kiwi, J., (1998), *Accelerated Photo-Oxidation of Concentrated p-Coumaric Acid in Homogeneous Solution. Mechanistic studies, Intermediates and Precursors Formed in the Dark*, Applied Catalysis B: Environmental, 17, 141-156.

[44] Walendziewski, J. and Trawczynski, J., (1996), *Alkylation of Toluene with Ethanol*, Ind. Eng. Chem. Res., 35, 3356-3361.

[45] Devlin, H.R. and Harris, I.J., (1984), *Mechanism of the Oxidation of Aqueous Phenol with Dissolved Oxygen*, Ind. Eng. Chem. Fundam., 23, 387-392.

[46] McKenna,E.A., Othoneos,A., Kiratzis,N. and Stoukides,M., (1993), *Synthesis of HCN in a Solid-Electrolyte-Cell Reactor*, Ind. Eng. Chem. Res., 32, 1104-1913.

[47] Waletzko, N. and Schmidt,L.D., (1988), *Modeling Catalytic Gauze Reactors: HCN Synthesis*, AIChE Journal, **34**, 7, 1146-1156.

[48] Hasenberg,D. and Schmidt,L.D., (1987), *HCN Synthesis from CH_4, NH_3 and O_2 on Clean Pt*, Journal of Catalysis, 104, 441-453.

[49] Hasenberg,D. and Schmidt,L.D., (1986), *HCN Synthesis from CH_4 and NH_3 on Platinum*, Journal of Catalysis, 97, 156-168.

[50] Hasenberg,D. and Schmidt,L.D., (1985), *HCN Synthesis from CH_4 and NH_3 on Clean Rh*, Journal of Catalysis, 91, 116-131.

[51] Lonyi, F., Engelhardt, J. and Kallo, D., (1991), *Para-selectivity of Toluene Ethylation over ZSM-5 Catalysts*, Zeolites, 11, 169-177.

[52] Paparatto, G., Moretti, E., Leofanti, G. and Gatti, F., (1987), *Toluene Ethylation on ZSM Zeolites*, J. Catalysis, 105, 227-232.

[53] Stull, D.R., Westrum Jr., E.F. and Sinke G.C., (1969), *The Chemical Thermodynamics of Organic Compounds*, John Wiley & Sons Inc., New York.

[54] Kirk, R.E. and Othmer, D.F., (1991a), *Encyclopedia of Chemical Technology*, 4ed, Vol 24., Wiley Interscience Publication, New York, 851-882.

[55] Kirk, R.E. and Othmer, D.F., (1991b), *Encyclopedia of Chemical Technology*, 4ed, Vol 7., Wiley Interscience Publication, New York, 753-782.

[56] Kirk, R.E. and Othmer, D.F., (1991c), *Encyclopedia of Chemical Technology*, 4ed, Vol 4., Wiley Interscience Publication, New York, 73-103.

[57] Kirk, R.E. and Othmer, D.F., (1991d), *Encyclopedia of Chemical Technology*, 4ed, Vol 5., Wiley Interscience Publication, New York, 1017-1072.

[58] McPherson,R.W., Starks,C.M. and Fryar,G.J., (1979), *Vinyl Chloride Monomer ... What you should know*, Hydrocarbon Processing, March, 75-88.

[59] Berg, L., (1969), *Azeotropic and Extractive Distillation: Selecting the Agent for Distillation*, Chem. Eng. Prog., **65**, 9, 52-57.

[60] Ewell, R.H., Harrison,J.M. and Berg,L., (1944), *Azeotropic Distillation*, Ind. Eng. Chem., **36**, 10, 871-875.

[61] Westerberg, A. and Wahnschafft, O., (1996), *Synthesis of Distillation-Based Separation Systems*, Advances in Chemical Engineering: Process Synthesis, 23, 71-72.

[62] Manzer,L.E., (1990), *The CFC-Ozone Issue: Progress on the Development of Alternatives to CFC'c*, Science, 249, 31-35.

[63] Ribeiro,F.H., Gerken,C.A., Rupprechter,G., Somorjai,G.A., Kellner,C.S., Coulston,G.W., Manzer,L.E. and Abrams,L., (1998), *Structure Insensitivity and Effect of Sulfur in the Reaction of Hydrodechlorination of 1,1-Dichlorotetrafluoethane (CF$_3$ − CFCl$_2$) over Pd Catalysts*, Journal of Catalysis, 176, 352-357.

[64] Reid, R.C., Prausnitz, J.M. and Poling, B.E., (1987), *The Properties of Gases & Liquids*, 4ed, Mc Graw Hill Book Co., 173-190.

[65] Benson,S.W., (1968), *Thermochemical Kinetics : Methods for the Estimation of Thermochemical Data and Rate Parameters*, John Wiley & Sons Inc., New York.

[66] Gani, R. and Fredenslund, Aa., (1993), *Computer Aided Molecular and Mixture Design with Specified Property Constraints*, Fluid Phase Equilibrium, 82, 39-46.

[67] , Gani, R. and Constantinou, L., (1996), *Molecular Structure Based Estimation of Properties for Process Design*, Fluid Phase Equilibrium, 116, 75-86.

[68] O'Connel,J.P. and Neurock,M., (1999), *Trends in Property Estimation for Process and Product Design*, Conference paper, FOCAPD '99 : Computer Aided Design for the 21st Century, July 18-23, Colorado, USA.

[69] Frurip,D., Rondan, N.G. and Storer, J.W., (1998), *Implementation and Application of Computational Thermochemistry to Industrial Process Design at the Dow Chemical Company*, Computational Thermochemistry: Prediction & Estimation of Molecular Thermodynamics, Am. Chem. Soc., 319-340.

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Appendix A

Joback Group Contribution Technique

Group contribution is a technique to predict the property of organic compounds with unknown and complex structure. The estimation method used in this task is developed by Joback[40]. The values of the critical properties and heat of formation can be estimated by summing up the difference (Δ) of the group contribution.

For critical properties and heat of formation, Joback proposed the following relations :

$$T_c = T_b \, [0.584 + 0.965 \sum \Delta_T - (\sum \Delta_T)^2 \,]^{-1}$$
$$P_c = (0.113 + 0.0032 n_A - \sum \Delta_P)^{-2}$$
$$V_c = 17.5 + \sum \Delta_V$$
$$\Delta H_f^o \,(298 \; K) = 68.29 + \sum_j n_j \Delta_H$$
$$\Delta G_f^o \,(298 \; K) = 53.88 + \sum_j n_j \Delta_G$$
$$C_p^o = (\sum_{j=1} n_j \Delta_a - 37.93) + (\sum_{j=1} n_j \Delta_b + 0.210)T +$$
$$(\sum_{j=1} n_j \Delta_c - 3.91 * 10^{-4})T^2 + (\sum_{j=1} n_j \Delta_d + 2.06 * 10^{-7})T^3$$

Table A.1: Joback's organic chemical groups

-CH3	> CH2	> CH − (nonring)	> C < (nonring)
=CH2	=CH- (non ring)	= C < (nonring)	=C=
=-CH	=-C-	-CH2-	> CH − (ring)
> C < (ring)	=CH- (ring)	= C < (ring)	-F
-Cl	-Br	-I	-OH (alcohol)
-OH (phenol)	-O- (non ring)	-O- (ring)	> C = O (nonring)
> C = O(ring)	O=CH-	-COOH	-COO-
=O	-NH2	> NH(nonring)	> NH(ring)
> N − (nonring)	-N= (non ring)	-N= (ring)	-CN
-NO2	-SH	-S- (non ring)	-S- (ring)

Joback's organic chemical groups are depicted in the following table.

Table A.2: Database of pure components with property values

'XXX'	Cpa	Cpb	Cpc	Cpd	Tc	Pc	Vc	Tb	g	h	no_atom
'H2O'	70.17	-0.208	4.015E-04	-2.096E-07	0.082	0.06	18	175.15	-282.68	-310.29	3
'CH4'	57.18	-0.158	4.029E-04	-2.173E-07	0.020	0.227	55	-86.35	-104.75	-143.19	5
'H2S'	69.87	-0.2086	4.153E-04	-2.1776E-07	0.373	89.4	99	15.5	-282.68	-310.29	3
'N2'	69.08	-0.224	4.178E-04	-2.1768E-07	0.021	0.16	20	-120.8	-53.88	-68.29	2
'O2'	66.04	-0.21	4.085E-04	-2.1665E-07	0.155	50.4	73	-107.8	-53.88	-68.29	2
'H2'	65.07	-0.201	3.772E-04	-1.984E-07	33.0	13.0	65	-177.6	-53.88	-68.29	2
'Cl2'	64.86	-0.176	3.523E-04	-1.905E-07	0.417	79.8	124	41.2	-53.88	-68.29	2
'Br2'	71.79	-0.1988	3.791E-04	-2.015E-07	0.588	103.2	127	133.9	-50.744	-37.36	2
'I2'	73.52	-0.2035	3.84E-04	-2.032E-07	0.819	0.0	155	259.50	-34.50	-5.82	2
'F2'	61.15	-0.1734	3.549E-04	-1.9396E-07	0.144	52.2	66	-113.00	-53.88	-68.29	2
'HCl'	68.60	-0.217	4.035E-04	-2.099E-07	0.325	83.1	81	-9.89	-149.21	-160.65	2
'HBr'	60.58	-0.220	4.082E-04	-2.1224E-07	0.363	85.5	0	8.80	-107.32	-104.55	2
'HI'	69.09	-0.2243	4.207E-04	-2.195E-07	0.424	83.1	0	39.60	-52.28	-41.91	2
'HF'	66.99	-0.21	3.89E-04	2.085E-07	0.461	64.8	69	95.00	-327.28	-339.59	2
'C6H6'	-2.14*6	6*5.74E-2	6*(-1.64E-6)	6*(-1.59E-8)	0.0082*6	0.0011*6	41*6	160.38	67.80	12.48	12
'NH3'	65.24	-0.187	4.081E-04	-2.179E-07	405.5	113.5	73	41.80	-70.04	-114.01	4
'HCN'	59.79	-0.150	3.414E-04	-1.879E-07	456.7	53.9	139	100.90	66.32	62.31	3
'CO2'	57.73	-0.137	3.3498E-04	-1.889E-07	304.1	73.8	94	-198.0	-448.48	-462.09	3
'CO'	68.80	-0.223	4.189E-04	-2.187E-07	132.9	35.0	93	-116.30	-191.28	-178.89	2
'CH2O'	61.41	-0.18	4.2085E-04	-1.83E-07	408.0	65.9	0	56.00	-163.88	-184.29	4
'HCOOH'	49.64	-0.07	4.75E-04	-1.86E-07	580.0	0.0	0	175.80	-405.08	-447.19	5
'N2O'	59.55	-0.137	4.49E-03	1.88E-06	431.0	101.0	168	96.3	103.65	81.53	3
'NO2'	62.16	-0.162	3.71E-4	-2.06E-7	431.0	101.0	168	96.3	-1.88	-34.32	3
'NO'	67.28	-0.211	4.01E-4	-2.11E-7	180.0	64.8	58	-76.6	32.87	22.01	2
'SO2'	61.15	-0.143	3.41E-4	-1.93E-7	430.8	78.8	122	65.2	-354.28	-365.49	3
'SO3'	57.14	-62.6	1.92E-4	-1.69E-7	491.0	82.1	127	120.0	-425.18	-464.29	4
'H2SO4'	83.24	-0.1046	4.196E-4	-2.608E-7	0.0	0.0	0	415.0	-741.44	-879.28	7

Table A.3: Database of functional groups with property values

'XXX'	Cpa	Cpb	Cpc	Cpd	Tc	Pc	Vc	Tb	g	h	no_atom
'COOH'	2.41E+1	4.27E-2	8.04E-5	-6.87E-8	0.0791	0.0077	89	169.09	-387.87	-426.72	4
'CN'	3.65E+1	-7.33E-2	1.84E-4	-1.03E-7	0.0496	-0.0101	91	125.66	89.22	88.43	2
'NH2'	2.69E+1	-4.12E-2	1.64E-4	-9.76E-8	0.0243	0.0109	38	73.23	14.07	-22.02	3
'NH'	-1.21	7.62E-2	-4.86E-5	1.05E-8	0.0295	0.0077	35	50.17	89.39	53.47	2
'NO2'	2.59E+1	-3.74E-3	1.29E-4	-8.88E-8	0.0437	0.0064	91	152.54	-16.83	-66.57	3
'C6H5'	-20.95	28.81E-2	-8.214E-6	-0.67E-8	0.0553	0.0063	237	164.66	110.55	56.88	11
'C6H4'	-25.06	23.16E-2	-6.59E-6	7.2E-8	0.0614	0.0060	228	168.94	153.30	101.22	10
'C6H3'	-31.17	47.52E-2	-4.31E-6	17.66E-8	0.0675	0.0057	219	173.22	196.05	145.56	10
'C6H2'	-37.28	5.19E-1	5.68E-4	30.3E-8	0.08	0.0054	210	177.5	238.8	189.9	8
'{OH}'	-2.81	1.11E-1	-1.16E-4	4.94E-8	0.0240	0.0184	-25	76.34	-197.37	-221.65	2
'OH'	2.5E+1	-6.91E-2	1.77E-4	-9.88E-8	0.0741	0.0112	28	92.88	-189.20	-208.04	2
'COO'	2.45E+1	4.02E-2	4.02E-5	-4.52E-8	0.0481	0.0005	82	81.1	-301.95	-337.92	3
'CHO'	3.09E+1	-3.36E-2	1.60E-4	-9.88E-8	0.0379	0.0030	82	72.24	-143.48	-162.03	3
'CO'	6.45	6.70E-2	-3.57E-5	2.88E-9	0.0380	0.0031	62	76.75	-120.50	-133.22	2
'ch:'	-2.14	5.74E-2	-1.64E-6	-1.59E-8	0.0100	0.0025	48	27.15	11.30	2.09	2
'c:'	-8.25	1.01E-1	-1.42E-4	6.78E-8	0.0143	0.0008	32	31.01	54.05	46.43	1
'ch2'	-6.03	8.54E-2	-8.00E-6	-1.80E-8	0.0100	0.0025	48	27.15	-3.68	-26.80	3
'ch'	-2.05E+1	1.62E-1	-1.60E-4	6.24E-8	0.0122	0.0004	38	21.78	40.99	8.67	2
'oh'	-2.81	1.11E-1	-1.16E-4	4.94E-8	0.0240	0.0184	-25	76.34	-197.37	-221.65	2
'co'	3.04E+1	-8.29E-2	2.36E-4	-1.31E-7	0.0284	0.0028	55	94.97	-126.27	-164.50	2
'nh'	1.18E+1	-2.30E-2	1.07E-4	-6.28E-8	0.0130	0.0114	29	52.82	75.61	31.65	2
'CH2:'	2.36E+1	-3.81E-2	1.72E-4	-1.03E-7	0.0113	-0.0028	56	18.18	3.77	-9.63	3
'CH:'	-8.0	1.05E-1	-9.63E-5	3.56E-8	0.0129	-0.0006	46	24.96	48.53	37.97	2
'C:'	-2.81E+1	2.08E-1	-3.06E-4	1.46E-7	0.0117	0.0011	38	24.14	92.36	83.99	1
'C*'	2.74E+1	-5.57E-2	1.01E-4	-5.02E-8	0.0026	0.0028	36	26.15	136.70	142.14	1

Table A.4: Database of functional groups with property values (continued)

'CH#'	2.45E+1	-2.71E-2	1.11E-4	-6.78E-8	0.0027	-0.0008	46	9.20	77.71	79.30	1
'C#'	7.87	2.01E-2	-8.33E-6	1.39E-9	0.0020	0.0016	37	27.38	109.82	115.51	1
'O:'	6.82	1.96E-2	1.27E-5	-1.78E-8	0.0143	0.0101	36	-10.50	-250.83	-247.61	1
'CH3'	1.95E+1	-8.08E-3	1.53E-4	-9.67E-8	0.0141	-0.0012	65	23.58	-43.96	-76.45	4
'CH2'	-9.09E-1	9.50E-2	-5.44E-5	1.19E-8	0.0189	0.0	56	22.88	8.42	-20.64	3
'CH'	-2.30E+1	2.04E-1	-2.65E-4	1.20E-7	0.0164	0.0020	41	21.74	58.36	29.89	2
'SH'	3.53E+1	-7.58E-2	1.85E-4	-1.03E-7	0.0031	0.0084	63	63.56	-22.99	-17.33	2
'SO2'	33.24	3.3598E-2	6.56E-5	-6.32E-8	0.0405	0.0251	126	47.78	-468.54	-453.35	3
'OSOO'	77.4	-11.241E-2	27.49E-5	-15.5E-8	0.0598	0.018	126	103.12	-427.71	-470.18	4
'osoo'	50.8	-1.121E-2	17.35E-5	-12.26E-8	0.0458	0.0246	116	120.72	-414.15	-482.06	4
'Cl'	3.33E+1	-9.63E-2	1.87E-4	-9.96E-8	0.0105	-0.0049	58	38.13	-64.31	-71.55	1
'Br'	2.86E+1	-6.49E-2	1.36E-4	-7.45E-8	0.0133	0.0057	71	66.86	-38.06	-29.48	1
'F'	2.65E+1	-9.13E-2	1.91E-4	-1.03E-7	0.0111	-0.0057	27	-0.03	-247.19	-251.92	1
'I'	3.21E+1	-6.41E-2	1.26E-4	-6.87E-8	0.0068	-0.0034	97	93.84	5.74	21.06	1
'O'	2.55E+1	-6.32E-2	1.11E-4	-5.48E-8	0.0168	0.0015	18	22.42	-105.0	-132.22	1
'S'	1.96E+1	-5.61E-3	4.02E-5	-2.76E-8	0.0119	0.0049	54	68.78	33.12	41.87	1
'C'	-6.62E+1	4.27E-1	-6.41E-4	3.01E-7	0.0067	0.0043	27	18.25	116.02	82.23	1
'N'	-3.11E+1	2.2E-1	-3.20E-4	1.46E-7	0.0169	0.0074	9	11.74	163.16	123.34	1
'H'	0.0	0.0	0.0	0.0	0.0	0.0	0	0.0	0.0	0.0	1
'c'	-9.09E+1	5.57E-1	-9.00E-4	4.69E-7	0.0042	0.0061	27	21.32	87.88	79.72	1
'o'	1.22E+1	-1.26E-2	6.03E-5	-3.86E-8	0.0098	0.0048	13	31.22	-98.22	-138.16	1
'n'	8.83	-3.84E-3	4.35E-5	-2.60E-8	0.0130	0.0114	29	52.82	79.93	55.52	1
's'	1.67E+1	4.81E-3	2.77E-5	-2.11E-8	0.0019	0.0051	38	52.10	27.76	39.10	1
'h'	0.0	0.0	0.0	0.0	0.0	0.0	0	0.0	0.0	0.0	1

Appendix B

Concept of Free Radicals

Free radicals are reactive intermediates having zero charge and tend to react with other unpaired electron species and form a new two-electron bond. Species possess an unpaired electron are of non-metallic elements such as carbon[35, 36]. The following is some structural types of radicals :

- simple alkyl radicals, $R_3\dot{C}$

- aryls, C_6H_5

- alkoxy, $R\dot{O}$

- hydroxyalkyl, $R\dot{C}HOH$

- haloalkyl, $Cl_3\dot{C}$

Radicals can be produced by several ways, among others :

- Thermolysis
  Thermolysis is the transfer of one electron (homolytic fission) of a covalent bond leads to a pair of radicals. Homolysis type requires little energy from the medium, occurs in gas phase or in solvents of low polarity. Heterolysis type prefers polar solvents in order to separate the ions.
  $R - R \rightarrow \dot{R} + \dot{R}$
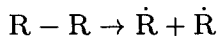
- Photolysis and Radiolysis
  Bond dissociation may take place by the addition of quantum energy of radiation whose electromagnetic radiation is related to wavelength. Acetone may be dissociated into methyl and acetyl radicals, central fragmentation of alkane and formation of hydxyl radical in aqueous solution.
  $CH_3CH_3CO \rightarrow \dot{C}H_3 + CH_3\dot{C}O$
  $n - C_4H_{10} \rightarrow n - C_4\dot{H}_{10} \rightarrow C_2\dot{H}_5 + C_2H_5^+$
  $H_2O \rightarrow H_2\dot{O}^+ \rightarrow \dot{R} + H_2O$
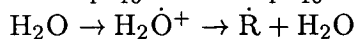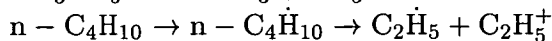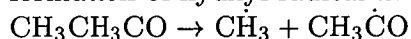
- Redox reaction
  Redox reaction involves the donation of one electron from aspin-paired molecule (reduction and oxidation respectively).
  $Ti^{2+} + H_2O_2 \rightarrow Ti^{3+} + O\dot{H} + OH^-$
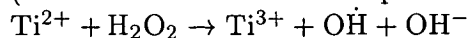
Fragmentation occurs in all possible ways predominates by those leading to the most stable free radicals. Stabilities of bonds affect the splitting patterns, which is shown in following order (the first is the most stable) :

- aromatics

- conjugated acyclic polyenes

- alicyclics

- n-hydrocarbons

- ketones

- ethers

- branched chain hydrocarbons

- alcohols

The ease of abstraction of hydrogen atoms in different classes of carbon atoms is relatively in the following order :

$$\text{tertiary} > \text{secondary} > \text{primary} > CH_4$$
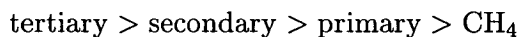
The ease of the formation of radicals is in conjunction with the stablility of the radicals.

The tendency of radicals to react follows the typical reactions such as :

- dimerization
  $Pb(CH_3)_4 \rightarrow Pb + 4C\dot{H}_3$
  $C\dot{H}_3 + C\dot{H}_3 \rightarrow CH_3CH_3$

- disproportionation and exchange
  $C\dot{H}_3 + H - CH_2Ph \rightarrow CH_4 + \dot{C}H_2Ph$
  $2\dot{C}H_2Ph \rightarrow PhCH_2CH_2Ph$

- Hydrogen addition to an unsaturated system
  Alkylation of olefin

- oxidation and reduction
  Spin trapping

Appendix C

Thermodynamic Requirements for Reactions

Thermodynamic criterion is applied to indicate whether a reaction could take place spontaneously. The criterion derives from the difference of free energy between products and reactants which must be negative. This means that the free energy of the products is lower than that of the reactants. The conversion of the reactants to products of the spontaneous reactions could go over 99 % when the equilibrium condition is reached. A reaction can go deliberately, but free energy must be added in order to overcome the enthalpy gain[37, 38].

Free energy (ΔG) is expressed in the following equation :

$$\Delta G = \Delta H - T\Delta S$$

Enthalpy changes (ΔH) in a reaction are concerned with the alteration in bond energies obtained by totalling all the bond energies involve in the reactants and products. Negative ΔH refers to exothermic reactions, while positive ΔH denotes endothermic reactions. Entropy changes (ΔS) are referred to the randomness of the system for which the less order a system the greater the entropy. A spontaneous reaction will prefer low or decreasing enthalpy and high or increasing entropy. In many cases, entropy has little effect in a spontaneous chemical reaction.

Free energies are also related to the equilibrium constant, associated with the following equation :

$$\Delta G = -2.303 \ R \ T \ \log \ K_{eq}$$

where: $R = 8.31917 \ J/(K.mol)$, T is the absolute temperature in K.

In general, the following conditions may be used as hints for spontaneous reactions.

1. Gases have higher entropies than liquids and solids. So the reactions of liquids to produce gases are more favourable.

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2. A molecule which cleaves into two or more parts affects the entropy changes. On the other hand, large increases in enthalpy frequently hamper the bond cleavage.

3. Entropy factor becomes more important as the temperature increases, while enthalpy does not directly depend on the absolute temperature.

The concept of free energy is used to predict equilibrium conditions of chemical reactions where optimum conversion can be attained. A reaction which is thermodynamically favourable from the negative free energy changes point of view may not be able to take place, unless certain preconditions are fulfilled. Conversely, a reaction which is thermodynamically unfavourable might occur when the condition changes. This phenomena can be explained by taking into account physical properties influencing chemical reactions. Variables considered under reaction environments include temperature, pressure, wavelength, surface type, species concentration, pH and participating species. In thermochemistry, temperature plays the most important role for it causes perturbation leading to thermal homolysis. At this stage, most chemical bonds will break to form radicals. There are significant entropy and enthalpy changes ensuing the increasing temperature which will result in negative free energy changes. Consequently physico-chemical data are essential when developing environment models for chemical reactions. The dependencies of the free energy on temperature can be found from the integration of the equilibrium equation and the heat capacities shown below.

Enthalpy can be expressed by the empirical correlation of heat capacities :

$$\frac{d\Delta H}{dT} = C_p$$

Heat capacity is a function of temperature having three different constants denoted as a, b and c (polynomial coefficients).

$$C_p = a + bT + cT^2$$

The integral of enthalpy in its correlation with heat capacity is :

$$\Delta H_{298K} - \Delta H_o = aT_{298K} + \frac{b}{2}T^2_{298K} + \frac{c}{3}T^3_{298K}$$

where ΔH_o is the constant of integration.

Entropy is also related to heat capacities by the following equation :

$$dS = C_p \, dlnT$$

Hence, the change of free energy with temperature is shown below as given in the Gibbs-Helmholtz equation :

$$\Delta G = \Delta H - T\frac{\Delta G}{dT}$$

By integration, the above equation gives a relation of heats of reaction or heats of formation and heat capacities only.

$$\Delta G = -\Delta H_o + aT_{opr}\ln T_{opr} + \tfrac{1}{2}bT_{opr}^2 + \tfrac{1}{6}cT_{opr}^3 + I/R\ T_{opr}$$

where I is the constant of integration and T_{opr} is the temperature of the operating condition, i.e. $T_{opr} > T_{298K}$.

The value of I can be determined by the equilibrium constant at single reference temperature, in most cases at 298 K.

$$I = \ln\ K_o - (-\tfrac{\Delta H_o}{RT_{298K}} + \tfrac{a}{R}\ln T_{298K} + \tfrac{1}{2}\tfrac{b}{R}T_{298K} + \tfrac{1}{6}\tfrac{c}{R}T_{298K}^2)$$

$$\ln\ K_o = \tfrac{-\Delta G_o}{RT_{298K}}$$

where ΔG_o and K_o are the reference condition taken at 298 K.

Appendix D

Deviation of Property Estimation Method Compared with Literature Data

Table D.1: Components' free energy value (kJ/mol)

Component	Joback Estimation	Literature	Absolute difference
CH_3F	-237.27	-210.1	27.17
CH_3Cl	-54.39	-62.93	8.54
CHF_3	-629.33	-662.8	33.47
$CHCl_3$	-80.69	-68.58	12.11
CCl_4	-87.34	-58.28	29.06
$CH_2{=}CHCl$	41.87	51.54	9.67
CH_3CCl_3	-66.99	-77.54	10.55
CH_3CF_3	-615.63	-679.2	63.57
CH_3CHCl_2	-60.34	-73.14	12.8
$ClCH_2CH_2Cl$	-57.9	-73.9	16
CH_3CHF_2	-426.1	-436.5	10.4
CH_3CH_2F	-228.85	-209.7	19.15
CH_3CH_2Cl	-45.97	-60.04	14.07
$CHClF_2$	-446.45	-470.9	24.45
$ClCH{=}CCl_2$	1.84	19.89	18.05
$CHCl_2F$	-263.57	-268.4	4.83
$CH_2{=}C{=}CH_2$	198.12	202.5	4.38
CH_3CH_3	-34.04	-32.95	1.09
$CH_2{=}CH_2$	61.42	68.16	6.74
$CH_3CH_2CH_2CH_3$	-8.78	-8.37	0.41
CH_3OH	-179.28	-162.6	16.68
C_4H_8	36.16	110.1	73.94
$CH_3CH_2COCH_2CH_3$	-137.7	-135.4	2.3
C_5H_{10}	35.48	38.6	3.12

Deviation of estimation method to literature data
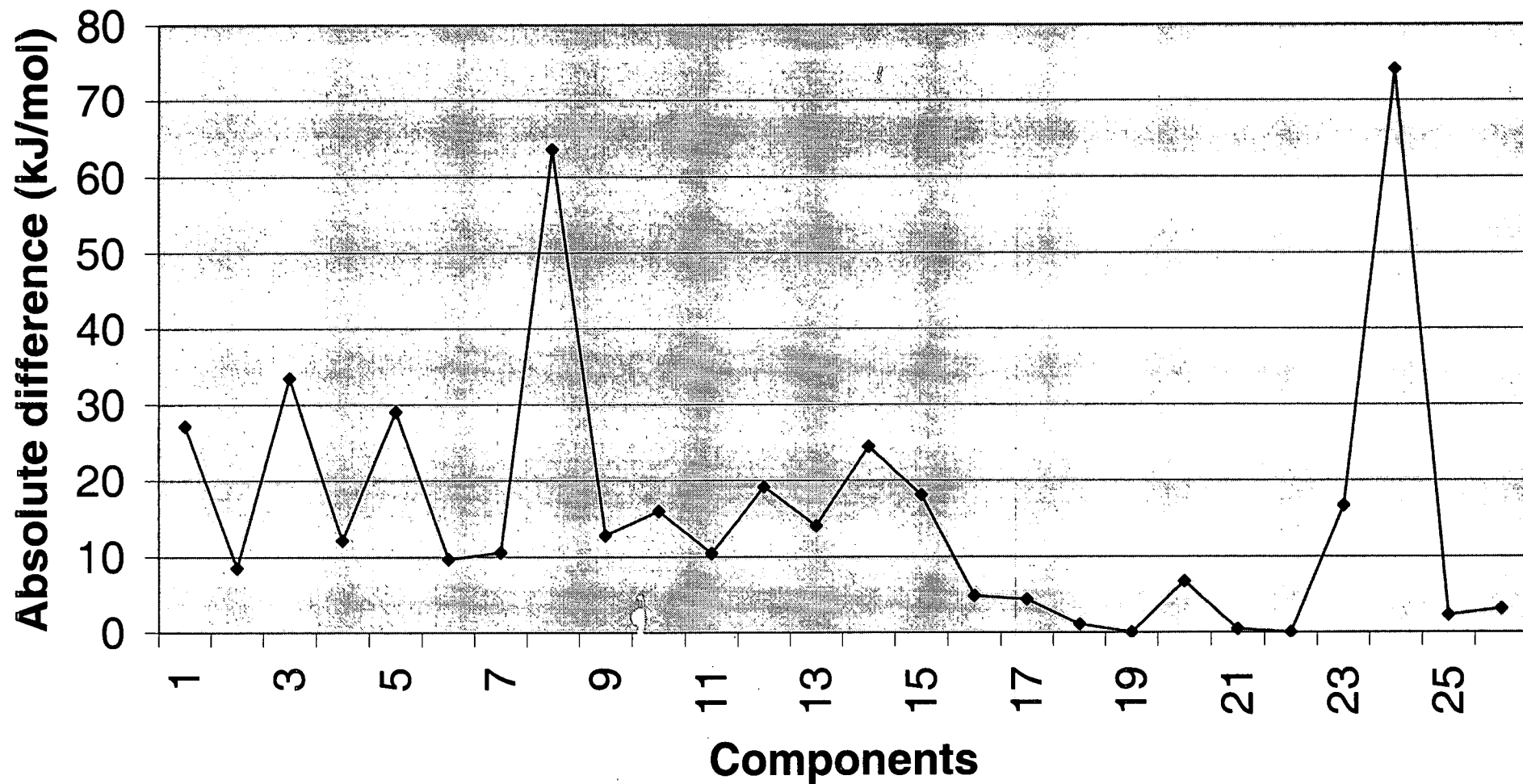
Gibbs free energy of components as a function of temperature

Chart: Free energy, kJ/mol (y-axis, from 2000 to -14000) versus Temperature, K (x-axis, values 298, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500)

Legend:
- CH3CH3
- ClCH2CHO
- ClCH:C:Cl2
- CH3CH2F
- CH2:CH:Cl
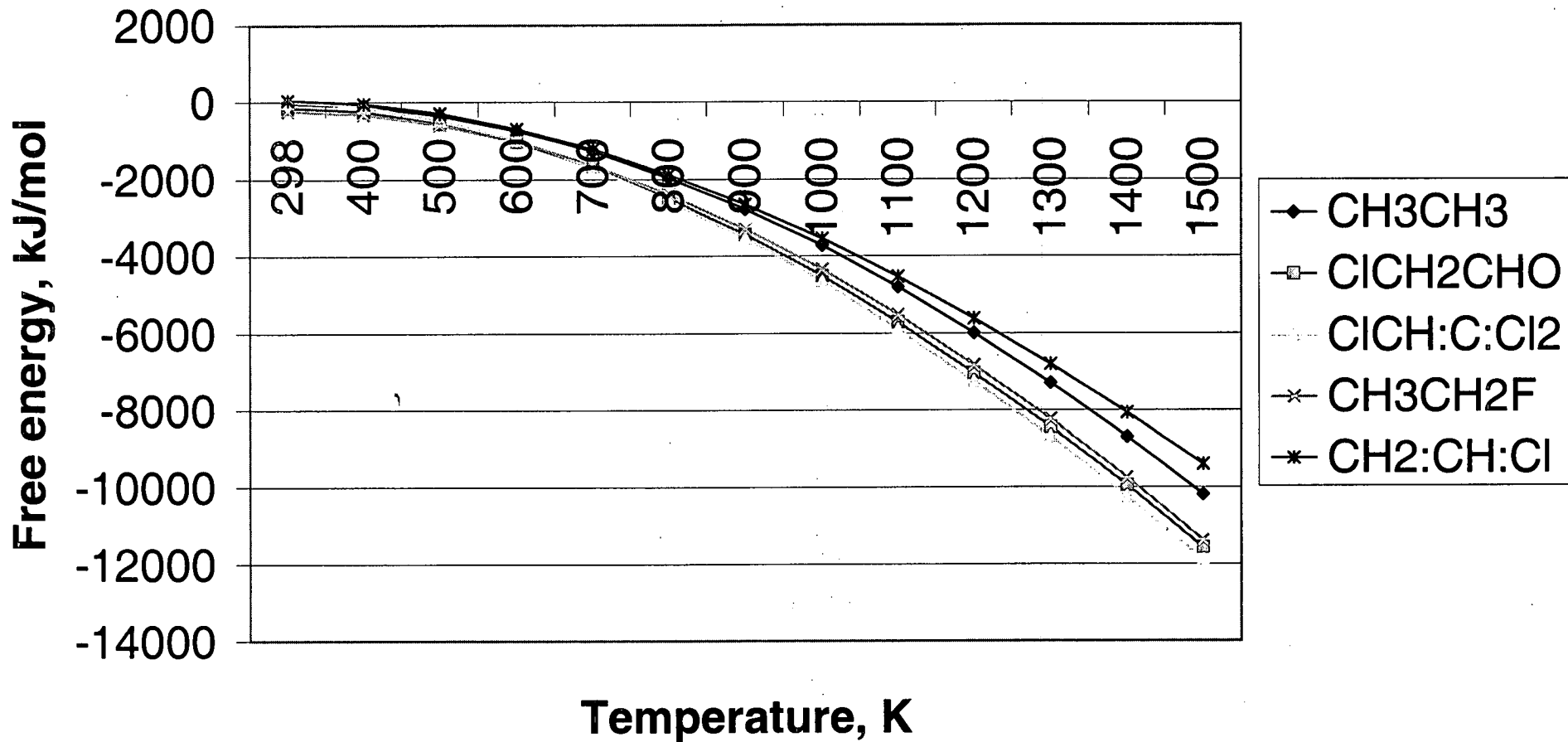
Appendix E

Intermediate Results Oxidation Reaction of p-Coumaric Acid

```
Number of reactants      3
{OH}C6H4CH:CH:COOH
O2
H2O
```

```
Radicals of component   {OH}C6H4CH:CH:COOH                        5
No. Radicals                      Valence Head      Radical    Radical
                                          position position-1 position-2
  1  CHCOOH                          -2      T          2          2
  2  {OH}C6H4CH                      -2      F          1          1
  3  {OH}C6H3CH:CH:COOH              -1      F          4          4
  4  {OH}C6H4CH:CH:                  -1      F          1          0
  5  C                              -4      T          1          0
```

```
Radicals of component   O2                                        1
No. Radicals                      Valence Head      Radical    Radical
                                          position position-1 position-2
  1  O                              -2      T          1          1
```

```
Radicals of component   H2O                                       2
No. Radicals                      Valence Head      Radical    Radical
                                          position position-1 position-2
  1  H                              -1      T          1          0
  2  HO                             -1      T          2          0
```

```
New products          11
            1      O2
            2      OHCH2COOH
            3      H2
            4      H2O
            5      {OH}C6H4CH2OH
```

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```
            6      {OH}C6H4CH:CH:COOH
            7      {OH}C6H4CH:CH2:
            8      CHOCOOH
            9      {OH}C6H4CHO
           10      CO2
           11      {OH}C6H4CH:CH:OH
```

Feasible reactions :
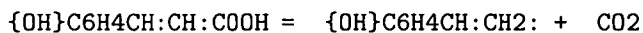
  {OH}C6H4CH:CH:COOH = {OH}C6H4CH:CH2: + CO2

     Free energy of reaction at 298 K is   -51.49 (kJ/mol)
        Enthalpy of reaction at 298 K is   -14.68 (kJ/mol)

***
  {OH}C6H4CH:CH:COOH + O2 = CHOCOOH + {OH}C6H4CHO
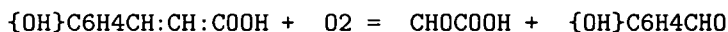
     Free energy of reaction at 298 K is   -330.14 (kJ/mol)
        Enthalpy of reaction at 298 K is   -331.71 (kJ/mol)

***

  Surviving species   4
           1   {OH}C6H4CH:CH2:
           2   CO2
           3   CHOCOOH
           4   {OH}C6H4CHO

Number of reactants   3
{OH}C6H4CH:CH2:
O2
H2O

Radicals of component   {OH}C6H4CH:CH2:   5

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	{OH}C6H4CHCH2	-2	F	1	2
2	H	-1	T	1	0
3	CH2	-2	T	1	1
4	{OH}C6H4CH	-2	F	1	1
5	{OH}C6H3CH:CH2:	-1	F	3	3

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

```
New products          12
            1     {OH}C6H4CH:CH2:
            2     O2
            3     {OH}C6H4[OH]CHCH3
            4     {OH}C6H4CH2CH2OH
            5     H2
            6     H2O
            7     CH3OH
            8     {OH}C6H4CH2OH
            9     CH2O
           10     {OH}C6H4CHO
           11     {OH}C6H4[OH]CHCH2OH
           12     {OH}{OH}C6H3CH:CH2:
```

Feasible reactions :
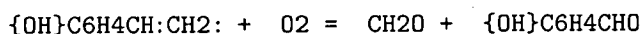
```
 {OH}C6H4CH:CH2: + O2 =  CH2O +  {OH}C6H4CHO              .
```

```
    Free energy of reaction at 298 K is    -305.78  (kJ/mol)
        Enthalpy of reaction at 298 K is    -306.37  (kJ/mol)
```

***
```
 {OH}C6H4CH:CH2: + H2O =  {OH}C6H4[OH]CHCH3
```

```
    Free energy of reaction at 298 K is       1.70  (kJ/mol)
        Enthalpy of reaction at 298 K is     -40.94  (kJ/mol)
```

***
```
 {OH}C6H4CH:CH2: + H2O =  {OH}C6H4CH2CH2OH
```

```
    Free energy of reaction at 298 K is       4.14  (kJ/mol)
        Enthalpy of reaction at 298 K is     -35.66  (kJ/mol)
```

***
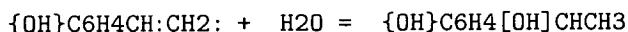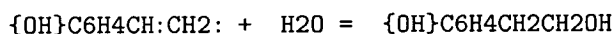
```
  Surviving species      4
            1     CH2O
            2     {OH}C6H4CHO
            3     {OH}C6H4[OH]CHCH3
            4     {OH}C6H4CH2CH2OH
```

```
Number of reactants      3
{OH}C6H4[OH]CHCH3
O2
H2O
```

```
Radicals of component     {OH}C6H4[OH]CHCH3                        5
No. Radicals                      Valence Head    Radical    Radical
                                  position position-1 position-2
  1  H                              -1     T        1          0
  2  {OH}C6H4CCH3                    -2     F        2          2
  3  {OH}C6H4CHOH                    -1     F        2          0
  4  CH3                            -1     T        1          0
```

```
5  C                              -4      T         1         1

Radicals of component     O2                                        1
No. Radicals                      Valence Head    Radical   Radical
                                          position position-1 position-2
1  O                              -2      T         1         1

Radicals of component     H2O                                       2
No. Radicals                      Valence Head    Radical   Radical
                                          position position-1 position-2
1  H                              -1      T         1         0
2  HO                             -1      T         2         0


New products           10
             1     H2
             2     O2
             3     H2O
             4     {OH}C6H4[OH]CHCH3
             5     {OH}C6H4CH2OH
             6     CH4
             7     {OH}C6H4COCH3
             8     CO2
             9     {OH}C6H4[OH][OH]CCH3
            10     CH3OH
```

Feasible reactions :

  {OH}C6H4[OH]CHCH3 = H2 + {OH}C6H4COCH3

    Free energy of reaction at   400.K is   -1.75 (kJ/mol)
       Enthalpy of reaction at   400.K is   1.56 (kJ/mol)

***
2 {OH}C6H4[OH]CHCH3 = {OH}C6H4CH2OH + CH4 + {OH}C6H4COCH3
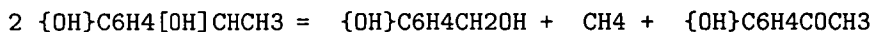
    Free energy of reaction at 298 K is   -46.51 (kJ/mol)
       Enthalpy of reaction at 298 K is   -4.05 (kJ/mol)

***
  {OH}C6H4[OH]CHCH3 + O2 = H2 + {OH}C6H4CH2OH + CO2

    Free energy of reaction at 298 K is   -400.58 (kJ/mol)
       Enthalpy of reaction at 298 K is   -367.88 (kJ/mol)

***

  Surviving species   5
             1   H2
             2   {OH}C6H4COCH3
             3   {OH}C6H4CH2OH
             4   CH4
             5   CO2

```
Number of reactants      3
{OH}C6H4CH2OH
O2
H2O
```

```
Radicals of component    {OH}C6H4CH2OH                              3
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2
  1  H                              -1      T        1          0
  2  {OH}C6H4CH                     -2      F        1          1
  3  {OH}C6H4C                      -3      F        1          0
```

```
Radicals of component    O2                                         1
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2
  1  O                              -2      T        1          1
```

```
Radicals of component    H2O                                        2
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2
  1  H                              -1      T        1          0
  2  HO                             -1      T        2          0
```

```
New products            6
              1    H2
              2    O2
              3    H2O
              4    {OH}C6H4CH2OH
              5    {OH}C6H4CHO
              6    {OH}C6H4COOH
```
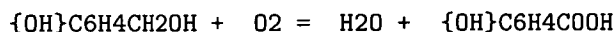
```
 Feasible reactions :

   {OH}C6H4CH2OH +  O2 =  H2O +  {OH}C6H4COOH

     Free energy of reaction at 298 K is    -435.89  (kJ/mol)
         Enthalpy of reaction at 298 K is    -440.04  (kJ/mol)


 ***

  Surviving species    2
           1    H2O
           2    {OH}C6H4COOH
```

```
Number of reactants      3
{OH}C6H4COOH
O2
H2O
```

```
Radicals of component    {OH}C6H4COOH                               2
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2
  1  {OH}C6H4                       -1      F        1          0
```

```
 2  C                          -4      T        1           0
```

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   6

```
            1      O2
            2      {OH}C6H5
            3      H2
            4      H2O
            5      CO2
            6      {OH}C6H4{OH}
```

Feasible reactions :

  {OH}C6H4COOH = {OH}C6H5 + CO2

```
     Free energy of reaction at 298 K is    -49.48  (kJ/mol)
         Enthalpy of reaction at 298 K is   -11.42  (kJ/mol)
```

***

```
  Surviving species      2
            1      {OH}C6H5
            2      CO2
```

Number of reactants   3
CHOCOOH
O2
H2O

Radicals of component   CHOCOOH   5

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 COCOOH	-1	T	2	0
3 CHO	-1	F	1	0
4 COOH	-1	T	1	0
5 C	-4	T	1	0

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

```
Radicals of component    H2O                                          2
No. Radicals                     Valence Head      Radical    Radical
                                         position position-1 position-2
  1  H                              -1    T            1          0
  2  HO                             -1    T            2          0

New products          7
              1      H2
              2      O2
              3      H2O
              4      CHOCOOH
              5      COOHCOOH
              6      CO2
              7      HCOOH


  Feasible reactions :

   CHOCOOH +  O2 =  H2O + 2 CO2

      Free energy of reaction at 298 K is    -540.53  (kJ/mol)
         Enthalpy of reaction at 298 K is    -509.14  (kJ/mol)


 ***
   CHOCOOH +  H2O =  H2 +  COOHCOOH

      Free energy of reaction at 298 K is     -15.59  (kJ/mol)
         Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)


 ***
   CHOCOOH +  H2O = 2 H2 + 2 CO2

      Free energy of reaction at 298 K is     -82.93  (kJ/mol)
         Enthalpy of reaction at 298 K is     -25.14  (kJ/mol)


 ***
   CHOCOOH +  H2O =  H2 +  CO2 +  HCOOH

      Free energy of reaction at 298 K is     -39.53  (kJ/mol)
         Enthalpy of reaction at 298 K is     -10.24  (kJ/mol)


 ***
   CHOCOOH +  H2O = 2 HCOOH

      Free energy of reaction at 298 K is       3.87  (kJ/mol)
         Enthalpy of reaction at 298 K is       4.66  (kJ/mol)


 ***

   Surviving species      5
              1      H2O
              2      CO2
              3      H2
              4      COOHCOOH
```
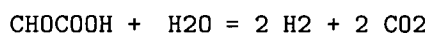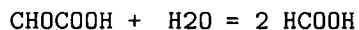
```
              5       HCOOH

Number of reactants       3
{OH}C6H4CHO
O2
H2O
```

Radicals of component	{OH}C6H4CHO			4
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 H		-1	T	1	0
2 {OH}C6H4CO		-1	F	1	0
3 {OH}C6H4		-1	F	1	0
4 C		-4	T	1	0

Radicals of component	O2			1
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 O		-2	T	1	1

Radicals of component	H2O			2
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 H		-1	T	1	0
2 HO		-1	T	2	0

```
New products          8
              1     H2
              2     O2
              3     H2O
              4     {OH}C6H4CHO
              5     {OH}C6H5
              6     CO2
              7     {OH}C6H4COOH
              8     {OH}C6H4{OH}


 Feasible reactions :

  {OH}C6H4CHO  +  O2  =  CO2  +  {OH}C6H4{OH}

     Free energy of reaction at 298 K is     -448.49  (kJ/mol)
        Enthalpy of reaction at 298 K is     -453.42  (kJ/mol)

 ***
  {OH}C6H4CHO  +  H2O  =  H2  +  {OH}C6H5  +  CO2

     Free energy of reaction at 298 K is      -65.07  (kJ/mol)
        Enthalpy of reaction at 298 K is      -34.11  (kJ/mol)

 ***
  {OH}C6H4CHO  +  H2O  =  H2  +  {OH}C6H4COOH

     Free energy of reaction at 298 K is      -15.59  (kJ/mol)
```
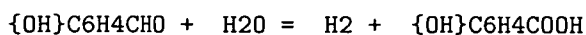
Enthalpy of reaction at 298 K is   -22.69 (kJ/mol)

***

Surviving species   5
```
          1     CO2
          2     {OH}C6H4{OH}
          3     H2
          4     {OH}C6H5
          5     {OH}C6H4COOH
```

Number of reactants   3
{OH}C6H4{OH}
O2
H2O

Radicals of component   {OH}C6H4{OH}   13

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 CH2:CH:CH:CH:CHCH2	-2	F	1	2
2 H	-1	T	1	0
3 CH2	-2	T	1	1
4 CH2:CH:CH:CH:CH	-2	F	1	1
5 CH:CH:CH:CH:	-2	T	1	4
6 CH:CH:	-2	T	1	2
7 CHCH	-4	F	1	2
8 CH2:CH:CHCHCH:CH2:	-2	F	3	4
9 CHCH:CH2:	-2	T	3	3
10 CH3CCH	-4	F	1	2
11 CH2CH:CH:CH:CH:CH2	-2	F	1	6
12 COCH:CH:CH:CO	-2	F	1	6
13 CHCOCH:CH:COCH	-4	F	1	6

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   25
```
          1     CH2:CH:CH:CH:CH:CH2:
          2     O2
          3     H2
          4     H2O
          5     CH3OH
          6     OHCH:CH:CH:CH2:
          7     OHCH:CH2:
          8     OHCH2CH2OH
          9     OHCH2CH:CH2:
```

```
10     CH3[OH]CHCH2OH
11     OHCH2CH:CH:CH:CH:CH3
12     CHOCH:CH:CH:CH:CHO
13     CH2O
14     CHOCHO
15     CHOCH:CH2:
16     CH3COCHO
17     CHOCOCH:CH:COCHO
18     OHCH:CH:CH:CH:OH
19     OHCH:CH:OH
20     OHCH2CH:CH:CH:CH:CH2OH
21     COOHCH:CH:CH:CH:COOH
22     COOHCH:CH:CH:CH:CHO
23     OHCH2CHO
24     CH3[OH]CHCHO
25     OHCH2COCH:CH:COCHO
```

Feasible reactions :

{OH}C6H4{OH} + O2 = H2 + CHOCOCH:CH:COCHO
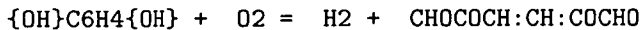
    Free energy of reaction at 298 K is   -189.46 (kJ/mol)
       Enthalpy of reaction at 298 K is   -172.48 (kJ/mol)

***
{OH}C6H4{OH} + O2 = COOHCH:CH:CH:CH:COOH

    Free energy of reaction at 298 K is   -340.18 (kJ/mol)
       Enthalpy of reaction at 298 K is   -359.48 (kJ/mol)

***
{OH}C6H4{OH} + O2 = OHCH2COCH:CH:COCHO
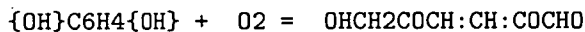
    Free energy of reaction at 298 K is   -226.76 (kJ/mol)
       Enthalpy of reaction at 298 K is   -239.13 (kJ/mol)

***
{OH}C6H4{OH} + O2 + H2O = CH2O + CHOCHO + CH3COCHO
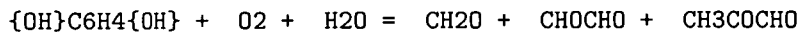
    Free energy of reaction at 298 K is   -180.78 (kJ/mol)
       Enthalpy of reaction at 298 K is   -159.39 (kJ/mol)

***

  Surviving species   7
            1   H2
            2   CHOCOCH:CH:COCHO
            3   COOHCH:CH:CH:CH:COOH
            4   OHCH2COCH:CH:COCHO
            5   CH2O
            6   CHOCHO
            7   CH3COCHO

```
Number of reactants      3
COOHCH:CH:CH:CH:COOH
O2
H2O
```

Radicals of component   COOHCH:CH:CH:CH:COOH   7

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	COOHCH:CH:CHCHCOOH	-2	F	2	3
2	H	-1	T	1	0
3	CHCOOH	-2	T	2	2
4	COOHCH:CH:CH	-2	F	1	1
5	COOHCH:CH:CH:CH:	-1	F	1	0
6	CH:CH:CH:CH:	-2	T	1	4
7	C	-4	T	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

```
New products        14
            1       COOHCH:CH:CH:CH:COOH
            2       O2
            3       COOHCH:CH:[OH]CHCH2COOH
            4       COOHCH:CH:CH2[OH]CHCOOH
            5       H2
            6       H2O
            7       OHCH2COOH
            8       COOHCH:CH:CH2OH
            9       COOHCH:CH:CH:CH2:
           10       OHCH:CH:CH:CH2:
           11       CHOCOOH
           12       COOHCH:CH:CHO
           13       CO2
           14       OHCH:CH:CH:CH:OH
```

```
  Feasible reactions :

   COOHCH:CH:CH:CH:COOH =  COOHCH:CH:CH:CH2: +  CO2

      Free energy of reaction at 298 K is    -51.49  (kJ/mol)
          Enthalpy of reaction at 298 K is   -14.68  (kJ/mol)

   ***
   COOHCH:CH:CH:CH:COOH +  O2 =  CHOCOOH +  COOHCH:CH:CHO
```

    Free energy of reaction at 298 K is   -330.14 (kJ/mol)
       Enthalpy of reaction at 298 K is   -331.71 (kJ/mol)

 ***
  COOHCH:CH:CH:CH:COOH + O2 = 2 CO2 + OHCH:CH:CH:CH:OH

    Free energy of reaction at 298 K is   -391.86 (kJ/mol)
       Enthalpy of reaction at 298 K is   -350.24 (kJ/mol)

 ***
  COOHCH:CH:CH:CH:COOH + H2O = COOHCH:CH:[OH]CHCH2COOH

    Free energy of reaction at 298 K is   9.32 (kJ/mol)
       Enthalpy of reaction at 298 K is   -32.73 (kJ/mol)

 ***
  COOHCH:CH:CH:CH:COOH + H2O = COOHCH:CH:CH2[OH]CHCOOH

    Free energy of reaction at 298 K is   9.32 (kJ/mol)
       Enthalpy of reaction at 298 K is   -32.73 (kJ/mol)

 ***
  COOHCH:CH:CH:CH:COOH + H2O = H2 + OHCH:CH:CH:CH2: + 2 CO2

    Free energy of reaction at 298 K is   -18.62 (kJ/mol)
       Enthalpy of reaction at 298 K is   52.20 (kJ/mol)

 ***
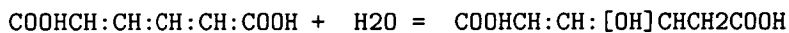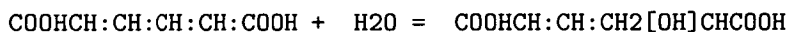
  Surviving species   9
            1   COOHCH:CH:CH:CH2:
            2   CO2
            3   CHOCOOH
            4   COOHCH:CH:CHO
            5   OHCH:CH:CH:CH:OH
            6   COOHCH:CH:[OH]CHCH2COOH
            7   COOHCH:CH:CH2[OH]CHCOOH
            8   H2
            9   OHCH:CH:CH:CH2:

Number of reactants   3
CHOCOCH:CH:COCHO
O2
H2O

Radicals of component   CHOCOCH:CH:COCHO   7
No. Radicals   Valence Head   Radical   Radical
                                        position position-1 position-2
 1 CHOCOCHCHCOCHO   -2   F   3   4
 2 H   -1   T   1   0
 3 CHCOCHO   -2   T   3   3
 4 CHOCOCH:CH:COCO   -1   F   1   0
 5 CHOCOCH:CH:CO   -1   F   1   0
 6 COCH:CH:CO   -2   T   1   4

| 7 | C | | -4 | T | 1 | 0 |

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

New products   15

1	CHOCOCH:CH:COCHO
2	O2
3	CHOCO[OH]CHCH2COCHO
4	CHOCOCH2[OH]CHCOCHO
5	H2
6	H2O
7	OHCH2COCHO
8	CHOCOCH:CH:CHO
9	CHOCH:CH:CHO
10	COOHCH:CH:CHO
11	CO2
12	CHOCO[OH]CH[OH]CHCOCHO
13	CHOCOCH:CH:COCOOH
14	CHOCOCH:CH:COOH
15	COOHCH:CH:COOH

Feasible reactions :

  CHOCOCH:CH:COCHO + O2 = CHOCH:CH:CHO + 2 CO2

    Free energy of reaction at 298 K is   -548.20 (kJ/mol)
      Enthalpy of reaction at 298 K is   -521.16 (kJ/mol)

***
  CHOCOCH:CH:COCHO + O2 = CO2 + CHOCOCH:CH:COOH

    Free energy of reaction at 298 K is   -518.49 (kJ/mol)
      Enthalpy of reaction at 298 K is   -525.27 (kJ/mol)

***
  CHOCOCH:CH:COCHO + H2O = CHOCO[OH]CHCH2COCHO

    Free energy of reaction at 298 K is   9.32 (kJ/mol)
      Enthalpy of reaction at 298 K is   -32.73 (kJ/mol)

***
  CHOCOCH:CH:COCHO + H2O = CHOCOCH2[OH]CHCOCHO
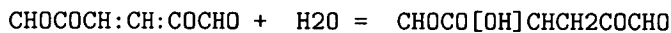
    Free energy of reaction at 298 K is   9.32 (kJ/mol)
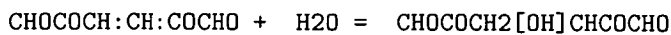
```
            Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)


***
  CHOCOCH:CH:COCHO +  H2O =  H2 +  CHOCOCH:CH:CHO +  CO2


    Free energy of reaction at 298 K is     -45.30  (kJ/mol)
        Enthalpy of reaction at 298 K is     -18.58  (kJ/mol)


***
  CHOCOCH:CH:COCHO +  H2O =  H2 +  CHOCOCH:CH:COCOOH


    Free energy of reaction at 298 K is     -15.59  (kJ/mol)
        Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)


***

  Surviving species      8
            1     CHOCH:CH:CHO
            2     CO2
            3     CHOCOCH:CH:COOH
            4     CHOCO[OH]CHCH2COCHO
            5     CHOCOCH2[OH]CHCOCHO
            6     H2
            7     CHOCOCH:CH:CHO
            8     CHOCOCH:CH:COCOOH


Number of reactants      3
COOHCH:CH:CH:CH2:
O2
H2O
```

```
Radicals of component    COOHCH:CH:CH:CH2:                       6
No. Radicals                      Valence Head    Radical   Radical
                                          position position-1 position-2
 1  COOHCH:CH:CHCH2                   -2      F        1         2
 2  H                                 -1      T        1         0
 3  CH2                               -2      T        1         1
 4  COOHCH:CH:CH                      -2      F        1         1
 5  CH:CH:CH:CH2:                     -1      T        4         0
 6  C                                 -4      T        1         0


Radicals of component    O2                                     1
No. Radicals                      Valence Head    Radical   Radical
                                          position position-1 position-2
 1  O                                 -2      T        1         1


Radicals of component    H2O                                    2
No. Radicals                      Valence Head    Radical   Radical
                                          position position-1 position-2
 1  H                                 -1      T        1         0
 2  HO                                -1      T        2         0


New products          14
            1     COOHCH:CH:CH:CH2:
```
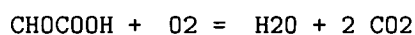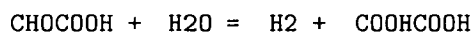
```
 2      O2
 3      COOHCH:CH:[OH]CHCH3
 4      COOHCH:CH:CH2CH2OH
 5      H2
 6      H2O
 7      CH3OH
 8      COOHCH:CH:CH2OH
 9      CH2:CH:CH:CH2:
10      CH2O
11      COOHCH:CH:CHO
12      CO2
13      COOHCH:CH:[OH]CHCH2OH
14      OHCH:CH:CH:CH2:
```

Feasible reactions :

COOHCH:CH:CH:CH2: = CH2:CH:CH:CH2: + CO2

    Free energy of reaction at 298 K is   -51.49 (kJ/mol)
      Enthalpy of reaction at 298 K is   -14.68 (kJ/mol)

***
COOHCH:CH:CH:CH2: + O2 = CH2O + COOHCH:CH:CHO

    Free energy of reaction at 298 K is   -305.78 (kJ/mol)
      Enthalpy of reaction at 298 K is   -306.37 (kJ/mol)

***
COOHCH:CH:CH:CH2: + H2O = COOHCH:CH:[OH]CHCH3

    Free energy of reaction at 298 K is   1.70 (kJ/mol)
      Enthalpy of reaction at 298 K is   -40.94 (kJ/mol)

***
COOHCH:CH:CH:CH2: + H2O = COOHCH:CH:CH2CH2OH

    Free energy of reaction at 298 K is   4.14 (kJ/mol)
      Enthalpy of reaction at 298 K is   -35.66 (kJ/mol)

***
COOHCH:CH:CH:CH2: + O2 + H2O = H2 + COOHCH:CH:CH2OH + CO2

    Free energy of reaction at 298 K is   -398.88 (kJ/mol)
      Enthalpy of reaction at 298 K is   -408.82 (kJ/mol)

***
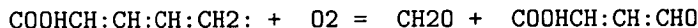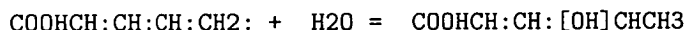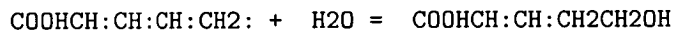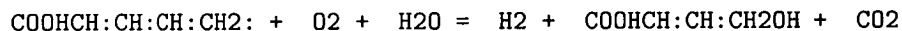
Surviving species   8
```
          1      CH2:CH:CH:CH2:
          2      CO2
          3      CH2O
          4      COOHCH:CH:CHO
          5      COOHCH:CH:[OH]CHCH3
```

```
        6      COOHCH:CH:CH2CH2OH
        7      H2
        8      COOHCH:CH:CH2OH
```

```
Number of reactants     3
CHOCOCH:CH:COCOOH
O2
H2O
```

Radicals of component   CHOCOCH:CH:COCOOH   9

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	CHOCOCHCHCOCOOH	-2	F	3	4
2	H	-1	T	1	0
3	CHCOCOOH	-2	T	3	3
4	CHOCOCH	-2	F	1	1
5	COCOCH:CH:COCOOH	-1	T	6	0
6	CHOCOCH:CH:CO	-1	F	1	0
7	COCH:CH:CO	-2	T	1	4
8	COCH:CH:COCOOH	-1	T	5	0
9	C	-4	T	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

```
New products           14
          1      CHOCOCH:CH:COCOOH
          2      O2
          3      H2
          4      H2O
          5      CHOCOCH2OH
          6      CHOCOCH:CH:CHO
          7      CHOCH:CH:CHO
          8      COOHCH:CH:CHO
          9      CHOCH:CH:COCOOH
         10      CO2
         11      COOHCOCH:CH:COCOOH
         12      CHOCOCH:CH:COOH
         13      COOHCH:CH:COOH
         14      COOHCH:CH:COCOOH
```
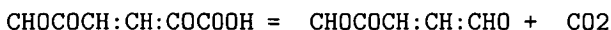
```
Feasible reactions :

  CHOCOCH:CH:COCOOH = CHOCOCH:CH:CHO +  CO2
```
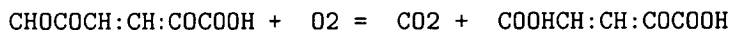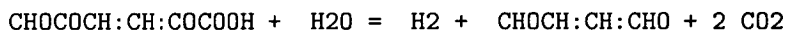
```
    Free energy of reaction at 298 K is     -29.71  (kJ/mol)
       Enthalpy of reaction at 298 K is       4.11  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  O2 =  COOHCH:CH:CHO + 2 CO2


    Free energy of reaction at 298 K is    -548.20  (kJ/mol)
       Enthalpy of reaction at 298 K is    -521.16  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  O2 =  CO2 +  COOHCH:CH:COCOOH


    Free energy of reaction at 298 K is    -518.49  (kJ/mol)
       Enthalpy of reaction at 298 K is    -525.27  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  H2O =  H2 +  CHOCH:CH:CHO + 2 CO2


    Free energy of reaction at 298 K is     -75.01  (kJ/mol)
       Enthalpy of reaction at 298 K is     -14.47  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  H2O =  H2 +  CHOCH:CH:COCOOH +  CO2


    Free energy of reaction at 298 K is     -45.30  (kJ/mol)
       Enthalpy of reaction at 298 K is     -18.58  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  H2O =  H2 +  CO2 +  CHOCOCH:CH:COOH


    Free energy of reaction at 298 K is     -45.30  (kJ/mol)
       Enthalpy of reaction at 298 K is     -18.58  (kJ/mol)


***
 CHOCOCH:CH:COCOOH +  H2O =  H2 +  COOHCOCH:CH:COCOOH


    Free energy of reaction at 298 K is     -15.59  (kJ/mol)
       Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)


***

 Surviving species      9
           1      CHOCOCH:CH:CHO
           2      CO2
           3      COOHCH:CH:CHO
           4      COOHCH:CH:COCOOH
           5      H2
           6      CHOCH:CH:CHO
           7      CHOCH:CH:COCOOH
           8      CHOCOCH:CH:COOH
           9      COOHCOCH:CH:COCOOH

Number of reactants      3
CHOCH:CH:CHO
```
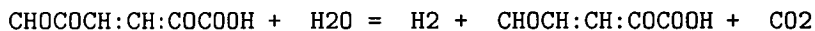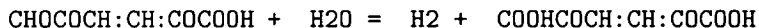
```
O2
H2O

Radicals of component     CHOCH:CH:CHO                              7
No. Radicals                        Valence Head      Radical    Radical
                                            position position-1 position-2
  1  CHOCHCHCHO                        -2      F          2          3
  2  H                                 -1      T          1          0
  3  CHCHO                             -2      T          2          2
  4  CHOCH:CH:CO                       -1      F          1          0
  5  CHOCH:CH:                         -1      F          1          0
  6  CH:CH:                            -2      T          1          2
  7  C                                 -4      T          1          0

Radicals of component     O2                                       1
No. Radicals                        Valence Head      Radical    Radical
                                            position position-1 position-2
  1  O                                 -2      T          1          1

Radicals of component     H2O                                      2
No. Radicals                        Valence Head      Radical    Radical
                                            position position-1 position-2
  1  H                                 -1      T          1          0
  2  HO                                -1      T          2          0

New products          15
              1    CHOCH:CH:CHO
              2    O2
              3    CHO[OH]CHCH2CHO
              4    CHOCH2[OH]CHCHO
              5    H2
              6    H2O
              7    OHCH2CHO
              8    CHOCH:CH2:
              9    OHCH:CH2:
             10    CHOCHO
             11    CO2
             12    CHO[OH]CH[OH]CHCHO
             13    CHOCH:CH:COOH
             14    CHOCH:CH:OH
             15    OHCH:CH:OH


 Feasible reactions :

  CHOCH:CH:CHO +  O2 = 2 CHOCHO

    Free energy of reaction at 298 K is    -330.14  (kJ/mol)
       Enthalpy of reaction at 298 K is    -331.71  (kJ/mol)

 ***
  CHOCH:CH:CHO +  O2 =  CO2 +  CHOCH:CH:OH

    Free energy of reaction at 298 K is    -440.32  (kJ/mol)
```
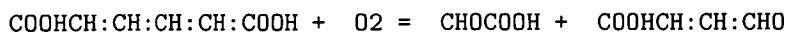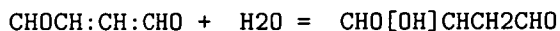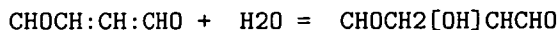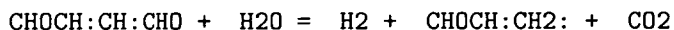
```
          Enthalpy of reaction at 298 K is     -439.81  (kJ/mol)

 ***
   CHOCH:CH:CHO  +  H2O =  CHO[OH]CHCH2CHO

     Free energy of reaction at 298 K is       9.32  (kJ/mol)
         Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

 ***
   CHOCH:CH:CHO  +  H2O =  CHOCH2[OH]CHCHO

     Free energy of reaction at 298 K is       9.32  (kJ/mol)
         Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

 ***
   CHOCH:CH:CHO  +  H2O =  H2 +  CHOCH:CH2: +  CO2

     Free energy of reaction at 298 K is     -67.08  (kJ/mol)
         Enthalpy of reaction at 298 K is     -37.37  (kJ/mol)

 ***
   CHOCH:CH:CHO  +  H2O =  H2 +  CHOCH:CH:COOH

     Free energy of reaction at 298 K is     -15.59  (kJ/mol)
         Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)

 ***

   Surviving species      8
              1      CHOCHO
              2      CO2
              3      CHOCH:CH:OH
              4      CHO[OH]CHCH2CHO
              5      CHOCH2[OH]CHCHO
              6      H2
              7      CHOCH:CH2:
              8      CHOCH:CH:COOH

Number of reactants      3
CHOCH:CH:COOH
O2
H2O

Radicals of component    CHOCH:CH:COOH                              9
No. Radicals                   Valence Head    Radical    Radical
                                       position position-1 position-2
 1  CHOCHCHCOOH                   -2     F         2          3
 2  H                            -1     T         1          0
 3  CHCOOH                       -2     T         2          2
 4  CHOCH                        -2     F         1          1
 5  COCH:CH:COOH                 -1     T         4          0
 6  CHOCH:CH:                    -1     F         1          0
 7  CH:CH:                       -2     T         1          2
 8  CH:CH:COOH                   -1     T         3          0
```
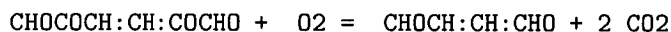
```
  9  C                                    -4       T         1          0
```

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   20

```
              1      CHOCH:CH:COOH
              2      O2
              3      CHO[OH]CHCH2COOH
              4      CHOCH2[OH]CHCOOH
              5      H2
              6      H2O
              7      OHCH2COOH
              8      CHOCH2OH
              9      CHOCH:CH2:
             10      OHCH:CH2:
             11      CH2:CH:COOH
             12      CHOCH:CH:CH:CH:COOH
             13      COOHCH:CH:CH:CH:COOH
             14      CHOCOOH
             15      CHOCHO
             16      CO2
             17      COOHCH:CH:COOH
             18      CHOCH:CH:OH
             19      OHCH:CH:OH
             20      OHCH:CH:COOH
```

Feasible reactions :
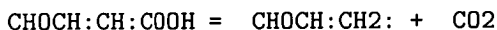
  CHOCH:CH:COOH = CHOCH:CH2: + CO2

```
     Free energy of reaction at 298 K is      -51.49  (kJ/mol)
        Enthalpy of reaction at 298 K is      -14.68  (kJ/mol)
```

  ***
  CHOCH:CH:COOH + O2 = OHCH:CH2: + 2 CO2
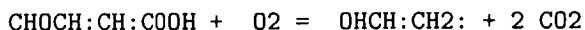
```
     Free energy of reaction at 298 K is     -491.81  (kJ/mol)
        Enthalpy of reaction at 298 K is     -454.49  (kJ/mol)
```

  ***
  CHOCH:CH:COOH + O2 = CHOCOOH + CHOCHO

```
     Free energy of reaction at 298 K is     -330.14  (kJ/mol)
        Enthalpy of reaction at 298 K is     -331.71  (kJ/mol)
```
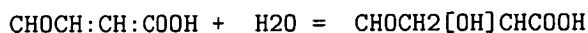
```
***
 CHOCH:CH:COOH +  O2 =  CO2 +  OHCH:CH:COOH

    Free energy of reaction at 298 K is    -440.32  (kJ/mol)
       Enthalpy of reaction at 298 K is    -439.81  (kJ/mol)

***
 CHOCH:CH:COOH +  H2O =  CHO[OH]CHCH2COOH

    Free energy of reaction at 298 K is       9.32  (kJ/mol)
       Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

***
 CHOCH:CH:COOH +  H2O =  CHOCH2[OH]CHCOOH

    Free energy of reaction at 298 K is       9.32  (kJ/mol)
       Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

***
 CHOCH:CH:COOH +  H2O =  H2 +  CH2:CH:COOH +  CO2

    Free energy of reaction at 298 K is     -67.08  (kJ/mol)
       Enthalpy of reaction at 298 K is     -37.37  (kJ/mol)

***
 CHOCH:CH:COOH +  H2O =  H2 +  COOHCH:CH:COOH

    Free energy of reaction at 298 K is     -15.59  (kJ/mol)
       Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)

***
 CHOCH:CH:COOH +  O2 +  H2O =  OHCH2COOH +  CHOCOOH

    Free energy of reaction at 298 K is    -383.03  (kJ/mol)
       Enthalpy of reaction at 298 K is    -421.05  (kJ/mol)

***

 Surviving species    12
            1     CHOCH:CH2:
            2     CO2
            3     OHCH:CH2:
            4     CHOCOOH
            5     CHOCHO
            6     OHCH:CH:COOH
            7     CHO[OH]CHCH2COOH
            8     CHOCH2[OH]CHCOOH
            9     H2
           10     CH2:CH:COOH
           11     COOHCH:CH:COOH
           12     OHCH2COOH

Number of reactants      3
```

```
COOHCH:CH:COOH
O2
H2O
```

Radicals of component   COOHCH:CH:COOH   6

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 COOHCHCHCOOH	-2	F	2	3
2 H	-1	T	1	0
3 CHCOOH	-2	T	2	2
4 COOHCH:CH:	-1	F	1	0
5 CH:CH:	-2	T	1	2
6 C	-4	T	1	0

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   14
```
           1      COOHCH:CH:COOH
           2      O2
           3      COOH[OH]CHCH2COOH
           4      COOHCH2[OH]CHCOOH
           5      H2
           6      H2O
           7      OHCH2COOH
           8      COOHCH:CH2:
           9      OHCH:CH2:
          10      COOHCH:CH:CH:CH:COOH
          11      CHOCOOH
          12      CO2
          13      COOHCH:CH:OH
          14      OHCH:CH:OH
```

Feasible reactions :

2 COOHCH:CH:COOH = H2 + COOHCH:CH:CH:CH:COOH + 2 CO2

       Free energy of reaction at 298 K is   -67.34 (kJ/mol)
          Enthalpy of reaction at 298 K is   -2.45 (kJ/mol)

***
  COOHCH:CH:COOH = COOHCH:CH2: + CO2

       Free energy of reaction at 298 K is   -51.49 (kJ/mol)
          Enthalpy of reaction at 298 K is   -14.68 (kJ/mol)
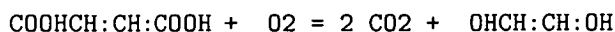
```
***
  COOHCH:CH:COOH +  O2 = 2 CHOCOOH

    Free energy of reaction at 298 K is    -330.14  (kJ/mol)
       Enthalpy of reaction at 298 K is    -331.71  (kJ/mol)

***
  COOHCH:CH:COOH +  O2 = 2 CO2 +  OHCH:CH:OH

    Free energy of reaction at 298 K is    -391.86  (kJ/mol)
       Enthalpy of reaction at 298 K is    -350.24  (kJ/mol)

***
  COOHCH:CH:COOH +  H2O =  COOH[OH]CHCH2COOH

    Free energy of reaction at 298 K is       9.32  (kJ/mol)
       Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

***
  COOHCH:CH:COOH +  H2O =  COOHCH2[OH]CHCOOH

    Free energy of reaction at 298 K is       9.32  (kJ/mol)
       Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

***
  COOHCH:CH:COOH +  H2O =  H2 +  OHCH:CH2: + 2 CO2

    Free energy of reaction at 298 K is     -18.62  (kJ/mol)
       Enthalpy of reaction at 298 K is      52.20  (kJ/mol)


***

  Surviving species      9
           1      H2
           2      COOHCH:CH:CH:CH:COOH
           3      CO2
           4      COOHCH:CH2:
           5      CHOCOOH
           6      OHCH:CH:OH
           7      COOH[OH]CHCH2COOH
           8      COOHCH2[OH]CHCOOH
           9      OHCH:CH2:

Number of reactants      3
COOHCH2[OH]CHCOOH
O2
H2O


Radicals of component    COOHCH2[OH]CHCOOH                        2
No. Radicals                    Valence Head   Radical   Radical
                                        position position-1 position-2
  1  H                             -1    T        1         0
  2  COOHCH2CCOOH                  -2    F        2         2
```

```
Radicals of component     O2                                          1
No. Radicals                         Valence Head    Radical   Radical
                                             position position-1 position-2
 1  O                                  -2     T        1          1

Radicals of component     H2O                                         2
No. Radicals                         Valence Head    Radical   Radical
                                             position position-1 position-2
 1  H                                  -1     T        1          0
 2  HO                                 -1     T        2          0

New products              6
                  1     H2
                  2     O2
                  3     H2O
                  4     COOHCH2[OH]CHCOOH
                  5     COOHCH2COCOOH
                  6     COOHCH2[OH][OH]CCOOH


  Feasible reactions :

   COOHCH2[OH]CHCOOH =  H2 +  COOHCH2COCOOH

     Free energy of reaction at    400.K is     -1.75  (kJ/mol)
        Enthalpy of reaction at    400.K is      1.56  (kJ/mol)

  ***

    Surviving species    2
                1     H2
                2     COOHCH2COCOOH

Number of reactants      3
COOHCH:CH2:
O2
H2O

Radicals of component     COOHCH:CH2:                                 6
No. Radicals                         Valence Head    Radical   Radical
                                             position position-1 position-2
 1  COOHCHCH2                          -2     F        1          2
 2  H                                  -1     T        1          0
 3  CH2                                -2     T        1          1
 4  COOHCH                             -2     F        1          1
 5  CH:CH2:                            -1     T        2          0
 6  C                                  -4     T        1          0

Radicals of component     O2                                          1
No. Radicals                         Valence Head    Radical   Radical
                                             position position-1 position-2
 1  O                                  -2     T        1          1
```
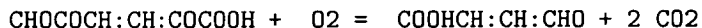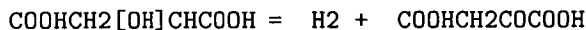
```
Radicals of component     H2O                                           2
No. Radicals                    Valence Head     Radical   Radical
                                        position position-1 position-2
 1  H                             -1     T           1         0
 2  HO                            -1     T           2         0


New products         15
             1      COOHCH:CH2:
             2      O2
             3      COOH[OH]CHCH3
             4      COOHCH2CH2OH
             5      H2
             6      H2O
             7      CH3OH
             8      COOHCH2OH
             9      CH2:CH2:
            10      CH2:CH:CH:CH2:
            11      CH2O
            12      COOHCHO
            13      CO2
            14      COOH[OH]CHCH2OH
            15      OHCH:CH2:
```

Feasible reactions :
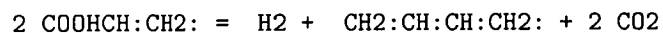
2 COOHCH:CH2: = H2 + CH2:CH:CH:CH2: + 2 CO2

```
      Free energy of reaction at 298 K is     -67.34  (kJ/mol)
         Enthalpy of reaction at 298 K is      -2.45  (kJ/mol)
```

***
 COOHCH:CH2: = CH2:CH2: + CO2

```
      Free energy of reaction at 298 K is     -51.49  (kJ/mol)
         Enthalpy of reaction at 298 K is     -14.68  (kJ/mol)
```

***
 COOHCH:CH2: + O2 = CH2O + COOHCHO

```
      Free energy of reaction at 298 K is    -305.78  (kJ/mol)
         Enthalpy of reaction at 298 K is    -306.37  (kJ/mol)
```

***
 COOHCH:CH2: + O2 = 2 CH2O + CO2
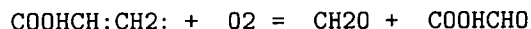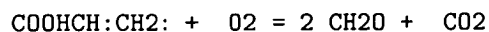
```
      Free energy of reaction at 298 K is    -332.91  (kJ/mol)
         Enthalpy of reaction at 298 K is    -295.71  (kJ/mol)
```
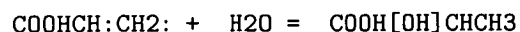
***
 COOHCH:CH2: + H2O = COOH[OH]CHCH3

```
      Free energy of reaction at 298 K is       1.70  (kJ/mol)
         Enthalpy of reaction at 298 K is     -40.94  (kJ/mol)
```
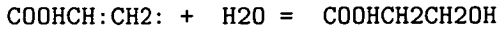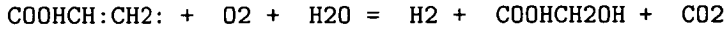
```
***
  COOHCH:CH2: +  H2O =  COOHCH2CH2OH

    Free energy of reaction at 298 K is       4.14  (kJ/mol)
       Enthalpy of reaction at 298 K is    -35.66  (kJ/mol)


***
  COOHCH:CH2: +  O2 +  H2O =  H2 +  COOHCH2OH +  CO2

    Free energy of reaction at 298 K is    -398.88  (kJ/mol)
       Enthalpy of reaction at 298 K is    -408.82  (kJ/mol)


***

  Surviving species      9
           1      H2
           2      CH2:CH:CH:CH2:
           3      CO2
           4      CH2:CH2:
           5      CH2O
           6      COOHCHO
           7      COOH[OH]CHCH3
           8      COOHCH2CH2OH
           9      COOHCH2OH


Number of reactants      3
COOHCH2COCOOH
O2
H2O


Radicals of component    COOHCH2COCOOH                              4
No. Radicals                       Valence Head    Radical    Radical
                                           position position-1 position-2
  1  COOHCH2CO                        -1      F        1          0
  2  CH2CO                            -2      T        1          2
  3  CH2COCOOH                        -1      T        3          0
  4  C                               -4      T        1          0


Radicals of component    O2                                        1
No. Radicals                       Valence Head    Radical    Radical
                                           position position-1 position-2
  1  O                                -2      T        1          1


Radicals of component    H2O                                       2
No. Radicals                       Valence Head    Radical    Radical
                                           position position-1 position-2
  1  H                                -1      T        1          0
  2  HO                               -1      T        2          0


New products             9
           1      O2
           2      COOHCH2CHO
           3      H2
```

```
             4      H2O
             5      OHCH2CHO
             6      CH3COOH
             7      CH3COCOOH
             8      CO2
             9      OHCH2COOH


 Feasible reactions :

   COOHCH2COCOOH =  COOHCH2CHO +  CO2

      Free energy of reaction at 298 K is     -29.71  (kJ/mol)
         Enthalpy of reaction at 298 K is       4.11  (kJ/mol)

 ***
   COOHCH2COCOOH =  CH3COCOOH +  CO2

      Free energy of reaction at 298 K is     -59.11  (kJ/mol)
         Enthalpy of reaction at 298 K is     -22.89  (kJ/mol)

 ***
   COOHCH2COCOOH +  O2 = 2 CO2 +  OHCH2COOH

      Free energy of reaction at 298 K is    -470.03  (kJ/mol)
         Enthalpy of reaction at 298 K is    -435.70  (kJ/mol)

 ***
   COOHCH2COCOOH +  H2O =  H2 +  OHCH2CHO + 2 CO2

      Free energy of reaction at 298 K is       3.16  (kJ/mol)
         Enthalpy of reaction at 298 K is      70.99  (kJ/mol)

 ***
   COOHCH2COCOOH +  H2O =  H2 +  CH3COOH + 2 CO2

      Free energy of reaction at 298 K is    -104.41  (kJ/mol)
         Enthalpy of reaction at 298 K is     -41.47  (kJ/mol)

 ***

   Surviving species      7
             1      COOHCH2CHO
             2      CO2
             3      CH3COCOOH
             4      OHCH2COOH
             5      H2
             6      OHCH2CHO
             7      CH3COOH

 Number of reactants      3
 COOHCH2CHO
 O2
 H2O
```

Radicals of component   COOHCH2CHO   6

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	COOHCH2CO	-1	F	1	0
3	COOHCH2	-1	F	1	0
4	CH2	-2	T	1	1
5	CH2CHO	-1	T	2	0
6	C	-4	T	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

New products   14

1	H2
2	O2
3	H2O
4	COOHCH2CHO
5	COOHCH3
6	CH3OH
7	CH3CHO
8	COOHCH2CH2COOH
9	COOHCH2CH2CHO
10	CH2O
11	CO2
12	COOHCH2COOH
13	COOHCH2OH
14	OHCH2CHO

Feasible reactions :
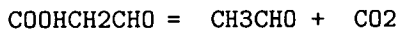
COOHCH2CHO = CH3CHO + CO2

    Free energy of reaction at 298 K is   -59.11 (kJ/mol)
      Enthalpy of reaction at 298 K is   -22.89 (kJ/mol)

***

2 COOHCH2CHO = COOHCH2CH2CHO + CH2O + CO2
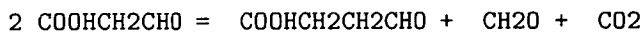
    Free energy of reaction at 298 K is   -27.13 (kJ/mol)
      Enthalpy of reaction at 298 K is   10.66 (kJ/mol)

***

COOHCH2CHO + O2 = H2 + CH2O + 2 CO2

```
      Free energy of reaction at 298 K is    -430.15  (kJ/mol)
          Enthalpy of reaction at 298 K is    -362.50  (kJ/mol)


  ***
   COOHCH2CHO +  O2 =  CH3OH + 2 CO2

      Free energy of reaction at 298 K is    -499.43  (kJ/mol)
          Enthalpy of reaction at 298 K is    -462.70  (kJ/mol)


  ***
   COOHCH2CHO +  O2 =  CO2 +  COOHCH2OH

      Free energy of reaction at 298 K is    -440.32  (kJ/mol)
          Enthalpy of reaction at 298 K is    -439.81  (kJ/mol)


  ***
   COOHCH2CHO +  H2O =  H2 +  COOHCH3 +  CO2

      Free energy of reaction at 298 K is     -74.70  (kJ/mol)
          Enthalpy of reaction at 298 K is     -45.58  (kJ/mol)


  ***
   COOHCH2CHO +  H2O =  H2 +  COOHCH2COOH

      Free energy of reaction at 298 K is     -15.59  (kJ/mol)
          Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)


  ***
   COOHCH2CHO +  H2O =  CH3OH +  CH2O +  CO2

      Free energy of reaction at   400.K is     -0.59  (kJ/mol)
          Enthalpy of reaction at   400.K is     -1.35  (kJ/mol)


  ***

   Surviving species      9
              1      CH3CHO
              2      CO2
              3      COOHCH2CH2CHO
              4      CH2O
              5      H2
              6      CH3OH
              7      COOHCH2OH
              8      COOHCH3
              9      COOHCH2COOH

Number of reactants      3
COOHCH2CH2CHO
O2
H2O

Radicals of component    COOHCH2CH2CHO                              6
No. Radicals                    Valence Head      Radical    Radical
```
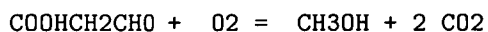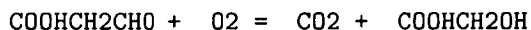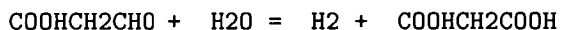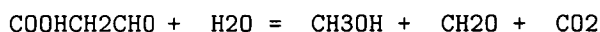
			position	position-1	position-2
1	H	-1	T	1	0
2	COOHCH2CH2CO	-1	F	1	0
3	COOHCH2CH2	-1	F	1	0
4	CH2CH2	-2	T	1	2
5	CH2CH2CHO	-1	T	3	0
6	C	-4	T	1	0

Radicals of component   O2   1

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

New products   15

1	H2
2	O2
3	H2O
4	COOHCH2CH2CHO
5	COOHCH2CH3
6	CH2:CH2:
7	OHCH2CH3
8	CH3CH2CHO
9	COOHCH2CH2CH2CH2COOH
10	COOHCH2CH2CH2CH2CHO
11	CO2
12	COOHCH2CH2COOH
13	COOHCH2CH2OH
14	OHCH2CH2OH
15	OHCH2CH2CHO

Feasible reactions :
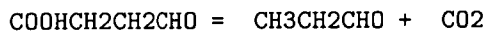
COOHCH2CH2CHO = CH3CH2CHO + CO2

Free energy of reaction at 298 K is   -59.11 (kJ/mol)
Enthalpy of reaction at 298 K is   -22.89 (kJ/mol)

***
COOHCH2CH2CHO + O2 = H2O + CH2:CH2: + 2 CO2

Free energy of reaction at 298 K is   -495.95 (kJ/mol)
Enthalpy of reaction at 298 K is   -418.83 (kJ/mol)
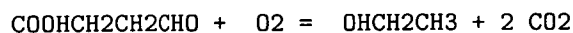
***
COOHCH2CH2CHO + O2 = OHCH2CH3 + 2 CO2

Free energy of reaction at 298 K is   -499.43 (kJ/mol)

Enthalpy of reaction at 298 K is   -462.70 (kJ/mol)

***
COOHCH2CH2CHO + O2 = CO2 + COOHCH2CH2OH

Free energy of reaction at 298 K is   -440.32 (kJ/mol)
Enthalpy of reaction at 298 K is   -439.81 (kJ/mol)

***
COOHCH2CH2CHO + H2O = H2 + COOHCH2CH3 + CO2

Free energy of reaction at 298 K is   -74.70 (kJ/mol)
Enthalpy of reaction at 298 K is   -45.58 (kJ/mol)

***
COOHCH2CH2CHO + H2O = H2 + COOHCH2CH2COOH

Free energy of reaction at 298 K is   -15.59 (kJ/mol)
Enthalpy of reaction at 298 K is   -22.69 (kJ/mol)

***
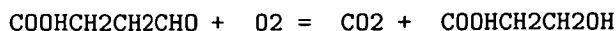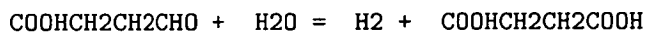
Surviving species   9 .
          1   CH3CH2CHO
          2   CO2
          3   H2O
          4   CH2:CH2:
          5   OHCH2CH3
          6   COOHCH2CH2OH
          7   H2
          8   COOHCH2CH3
          9   COOHCH2CH2COOH

Number of reactants   3
COOHCH:CH:COCOOH
O2
H2O

Radicals of component   COOHCH:CH:COCOOH   8
No. Radicals   Valence Head   Radical   Radical
                                        position position-1 position-2
1   COOHCHCHCOCOOH   -2   F   3   4
2   H   -1   T   1   0
3   CHCOCOOH   -2   T   3   3
4   COOHCH   -2   F   1   1
5   COOHCH:CH:CO   -1   F   1   0
6   CH:CH:CO   -2   T   1   3
7   CH:CH:COCOOH   -1   T   4   0
8   C   -4   T   1   0

Radicals of component   O2   1
No. Radicals   Valence Head   Radical   Radical
                                        position position-1 position-2
1   O   -2   T   1   1

```
Radicals of component    H2O                                       2
No. Radicals                    Valence Head    Radical   Radical
                                        position position-1 position-2
 1  H                             -1      T          1          0
 2  HO                            -1      T          2          0

New products        12
            1       COOHCH:CH:COCOOH
            2       O2
            3       H2
            4       H2O
            5       COOHCH2OH
            6       COOHCH:CH:CHO
            7       OHCH:CH:CHO
            8       CH2:CH:COCOOH
            9       COOHCHO
           10       CO2
           11       COOHCH:CH:COOH
           12       OHCH:CH:COOH
```
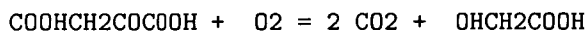
Feasible reactions :

  COOHCH:CH:COCOOH = COOHCH:CH:CHO + CO2

     Free energy of reaction at 298 K is   -29.71 (kJ/mol)
        Enthalpy of reaction at 298 K is   4.11 (kJ/mol)

***
  COOHCH:CH:COCOOH = CH2:CH:COCOOH + CO2

     Free energy of reaction at 298 K is   -51.49 (kJ/mol)
        Enthalpy of reaction at 298 K is   -14.68 (kJ/mol)

***
  COOHCH:CH:COCOOH + O2 = 2 CO2 + OHCH:CH:COOH

     Free energy of reaction at 298 K is   -470.03 (kJ/mol)
        Enthalpy of reaction at 298 K is   -435.70 (kJ/mol)

***
  COOHCH:CH:COCOOH + H2O = H2 + OHCH:CH:CHO + 2 CO2

     Free energy of reaction at 298 K is   3.16 (kJ/mol)
        Enthalpy of reaction at 298 K is   70.99 (kJ/mol)

***
  COOHCH:CH:COCOOH + H2O = H2 + CO2 + COOHCH:CH:COOH

     Free energy of reaction at 298 K is   -45.30 (kJ/mol)
        Enthalpy of reaction at 298 K is   -18.58 (kJ/mol)

***
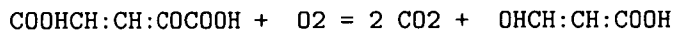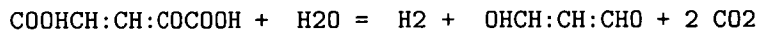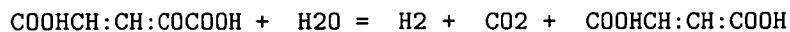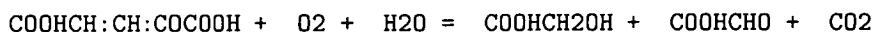
```
     COOHCH:CH:COCOOH  +  O2  +  H2O  =  COOHCH2OH  +  COOHCHO  +  CO2

        Free energy of reaction at 298 K is     -412.74  (kJ/mol)
           Enthalpy of reaction at 298 K is     -416.94  (kJ/mol)


  ***

    Surviving species       9
                1       COOHCH:CH:CHO
                2       CO2
                3       CH2:CH:COCOOH
                4       OHCH:CH:COOH
                5       H2
                6       OHCH:CH:CHO
                7       COOHCH:CH:COOH
                8       COOHCH2OH
                9       COOHCHO


  Number of reactants      3
  CHOCOCH:CH:COOH
  O2
  H2O


  Radicals of component    CHOCOCH:CH:COOH                           9
  No. Radicals                    Valence Head     Radical    Radical
                                          position position-1 position-2

    1  CHOCOCHCHCOOH                 -2      F         2          3
    2  H                            -1      T         1          0
    3  CHCOOH                       -2      T         2          2
    4  CHOCOCH                      -2      F         1          1
    5  COCOCH:CH:COOH               -1      T         5          0
    6  CHOCOCH:CH:                  -1      F         1          0
    7  COCH:CH:                     -2      T         1          3
    8  COCH:CH:COOH                 -1      T         4          0
    9  C                            -4      T         1          0


  Radicals of component    O2                                       1
  No. Radicals                    Valence Head     Radical    Radical
                                          position position-1 position-2

    1  O                            -2      T         1          1


  Radicals of component    H2O                                      2
  No. Radicals                    Valence Head     Radical    Radical
                                          position position-1 position-2

    1  H                            -1      T         1          0
    2  HO                           -1      T         2          0


  New products           16
                1       CHOCOCH:CH:COOH
                2       O2
                3       H2
                4       H2O
                5       OHCH2COOH
                6       CHOCOCH2OH
```

```
        7       CHOCOCH:CH2:
        8       CHOCH:CH2:
        9       COOHCH:CH2:
       10       CHOCH:CH:COOH
       11       CHOCOOH
       12       CO2
       13       COOHCOCH:CH:COOH
       14       CHOCOCH:CH:OH
       15       COOHCH:CH:OH
       16       COOHCH:CH:COOH
```

Feasible reactions :

 CHOCOCH:CH:COOH = CHOCOCH:CH2: + CO2

    Free energy of reaction at 298 K is   -51.49 (kJ/mol)
       Enthalpy of reaction at 298 K is   -14.68 (kJ/mol)

***
 CHOCOCH:CH:COOH + O2 = COOHCH:CH2: + 2 CO2
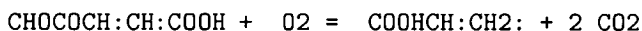
    Free energy of reaction at 298 K is   -569.98 (kJ/mol)
       Enthalpy of reaction at 298 K is   -539.95 (kJ/mol)
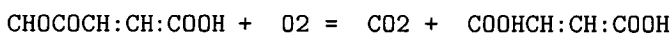
***
 CHOCOCH:CH:COOH + O2 = CO2 + COOHCH:CH:COOH

    Free energy of reaction at 298 K is   -518.49 (kJ/mol)
       Enthalpy of reaction at 298 K is   -525.27 (kJ/mol)

***
 CHOCOCH:CH:COOH + H2O = H2 + CHOCH:CH2: + 2 CO2
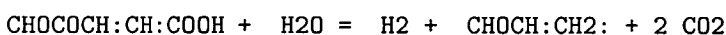
    Free energy of reaction at 298 K is   -96.79 (kJ/mol)
       Enthalpy of reaction at 298 K is   -33.26 (kJ/mol)

***
 CHOCOCH:CH:COOH + H2O = H2 + CHOCH:CH:COOH + CO2

    Free energy of reaction at 298 K is   -45.30 (kJ/mol)
       Enthalpy of reaction at 298 K is   -18.58 (kJ/mol)

***
 CHOCOCH:CH:COOH + H2O = H2 + COOHCOCH:CH:COOH

    Free energy of reaction at 298 K is   -15.59 (kJ/mol)
       Enthalpy of reaction at 298 K is   -22.69 (kJ/mol)

***
 CHOCOCH:CH:COOH + H2O = COOHCH:CH2: + CHOCOOH
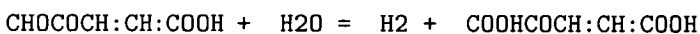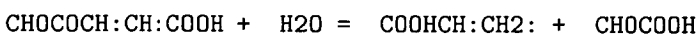
    Free energy of reaction at 298 K is   -29.45 (kJ/mol)
       Enthalpy of reaction at 298 K is   -30.81 (kJ/mol)

```
***

  Surviving species      9
          1     CHOCOCH:CH2:
          2     CO2
          3     COOHCH:CH2:
          4     COOHCH:CH:COOH
          5     H2
          6     CHOCH:CH2:
          7     CHOCH:CH:COOH
          8     COOHCOCH:CH:COOH
          9     CHOCOOH

Number of reactants      3
OHCH:CH:CH:CH:OH
O2
H2O


Radicals of component    OHCH:CH:CH:CH:OH                        7
No. Radicals                    Valence Head   Radical    Radical
                                        position position-1 position-2
  1  OHCH:CH:CHCHOH                 -2     F        2         3
  2  H                             -1     T        1         0
  3  CHOH                          -2     T        2         2
  4  OHCH:CH:CH                    -2     F        1         1
  5  CH:CH:CH:CH:                  -2     T        1         4
  6  OH                            -1     T        1         0
  7  CH2CH:CH:CH2                  -2     T        1         4


Radicals of component    O2                                     1
No. Radicals                    Valence Head   Radical    Radical
                                        position position-1 position-2
  1  O                            -2     T        1         1


Radicals of component    H2O                                    2
No. Radicals                    Valence Head   Radical    Radical
                                        position position-1 position-2
  1  H                            -1     T        1         0
  2  HO                           -1     T        2         0


New products             9
          1     O2
          2     H2
          3     H2O
          4     OHCH:CH:CH2OH
          5     OHCH:CH:CH:CH2:
          6     OHCH2CH:CH:CH3
          7     HCOOH
          8     OHCH:CH:CH:CH:OH
          9     OHCH2CH:CH:CH2OH


  Feasible reactions :
```

```
   Surviving species      0

Number of reactants     3
OHCH:CH2:
O2
H2O
```

```
Radicals of component    OHCH:CH2:                              4
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2

   1  OHCHCH2                        -2      F        1          2
   2  H                             -1      T        1          0
   3  CH2                           -2      T        1          1
   4  OHCH                          -2      F        1          1
```

```
Radicals of component    O2                                     1
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2

   1  O                            -2      T        1          1
```

```
Radicals of component    H2O                                    2
No. Radicals                      Valence Head    Radical    Radical
                                          position position-1 position-2

   1  H                            -1      T        1          0
   2  HO                           -1      T        2          0
```

```
New products              8
                  1      OHCH:CH2:
                  2      O2
                  3      OHCH2CH2OH
                  4      H2
                  5      H2O
                  6      CH3OH
                  7      CH2O
                  8      HCOOH
```
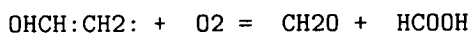
```
  Feasible reactions :

  OHCH:CH2: +  O2 =  CH2O +   HCOOH

     Free energy of reaction at 298 K is   -378.18  (kJ/mol)
        Enthalpy of reaction at 298 K is   -383.49  (kJ/mol)

  ***
  OHCH:CH2: +  H2O =  OHCH2CH2OH

     Free energy of reaction at 298 K is      4.14  (kJ/mol)
        Enthalpy of reaction at 298 K is    -35.66  (kJ/mol)

  ***
```
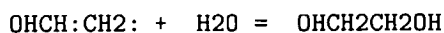
```
   Surviving species      3
              1       CH2O
              2       HCOOH
              3       OHCH2CH2OH


Number of reactants       3
OHCH:CH:COOH
O2
H2O
```

```
Radicals of component      OHCH:CH:COOH                              6
No. Radicals                    Valence Head       Radical    Radical
                                        position position-1 position-2
  1  OHCHCHCOOH                    -2      F          2          3
  2  H                            -1      T          1          0
  3  CHCOOH                        -2      T          2          2
  4  OHCH                          -2      F          1          1
  5  OHCH:CH:                      -1      F          1          0
  6  C                            -4      T          1          0
```

```
Radicals of component      O2                                       1
No. Radicals                    Valence Head       Radical    Radical
                                        position position-1 position-2
  1  O                            -2      T          1          1
```

```
Radicals of component      H2O                                      2
No. Radicals                    Valence Head       Radical    Radical
                                        position position-1 position-2
  1  H                            -1      T          1          0
  2  HO                           -1      T          2          0
```

```
New products          12
              1       OHCH:CH:COOH
              2       O2
              3       OHCH2[OH]CHCOOH
              4       H2
              5       H2O
              6       OHCH2COOH
              7       OHCH:CH2:
              8       OHCH:CH:CH:CH:OH
              9       CHOCOOH
             10       HCOOH
             11       CO2
             12       OHCH:CH:OH
```

```
  Feasible reactions :

  2 OHCH:CH:COOH =  H2 +  OHCH:CH:CH:CH:OH + 2 CO2

      Free energy of reaction at 298 K is     -67.34  (kJ/mol)
         Enthalpy of reaction at 298 K is      -2.45  (kJ/mol)


  ***
```
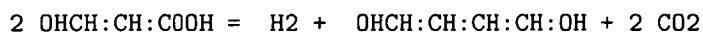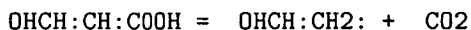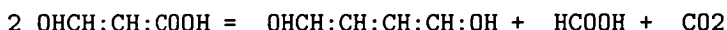
```
OHCH:CH:COOH  =  OHCH:CH2:  +  CO2

   Free energy of reaction at 298 K is     -51.49  (kJ/mol)
      Enthalpy of reaction at 298 K is     -14.68  (kJ/mol)

***
2 OHCH:CH:COOH  =  OHCH:CH:CH:CH:OH  +  HCOOH  +  CO2

   Free energy of reaction at 298 K is     -23.94  (kJ/mol)
      Enthalpy of reaction at 298 K is      12.45  (kJ/mol)

***
 OHCH:CH:COOH  +  O2  =  H2  +  CHOCOOH  +  CO2

   Free energy of reaction at 298 K is    -445.94  (kJ/mol)
      Enthalpy of reaction at 298 K is    -423.73  (kJ/mol)

***
 OHCH:CH:COOH  +  O2  =  OHCH2COOH  +  CO2

   Free energy of reaction at 298 K is    -483.24  (kJ/mol)
      Enthalpy of reaction at 298 K is    -490.38  (kJ/mol)

***
 OHCH:CH:COOH  +  O2  =  CHOCOOH  +  HCOOH

   Free energy of reaction at 298 K is    -402.54  (kJ/mol)
      Enthalpy of reaction at 298 K is    -408.83  (kJ/mol)

***
 OHCH:CH:COOH  +  H2O  =  OHCH2[OH]CHCOOH

   Free energy of reaction at 298 K is       9.32  (kJ/mol)
      Enthalpy of reaction at 298 K is     -32.73  (kJ/mol)

***
 OHCH:CH:COOH  +  O2  +  H2O  =  3 HCOOH

   Free energy of reaction at 298 K is    -398.67  (kJ/mol)
      Enthalpy of reaction at 298 K is    -404.17  (kJ/mol)

***

  Surviving species      8
            1      H2
            2      OHCH:CH:CH:CH:OH
            3      CO2
            4      OHCH:CH2:
            5      HCOOH
            6      CHOCOOH
            7      OHCH2COOH
            8      OHCH2[OH]CHCOOH

Number of reactants      3
```
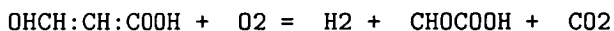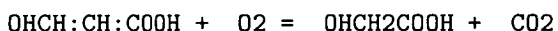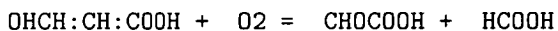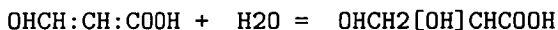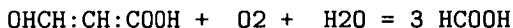
```
CHOCH:CH:OH
O2
H2O
```

Radicals of component   CHOCH:CH:OH   7

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	CHOCHCHOH	-2	F	2	3
2	H	-1	T	1	0
3	CHOH	-2	T	2	2
4	CHOCH	-2	F	1	1
5	COCH:CH:OH	-1	T	4	0
6	CH:CH:OH	-1	T	3	0
7	C	-4	T	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

```
New products        13
            1     CHOCH:CH:OH
            2     O2
            3     CHO[OH]CHCH2OH
            4     H2
            5     H2O
            6     CHOCH2OH
            7     CH2:CH:OH
            8     OHCH:CH:CH:CH:OH
            9     HCOOH
           10     CHOCHO
           11     CO2
           12     COOHCH:CH:OH
           13     OHCH:CH:OH
```

Feasible reactions :

  CHOCH:CH:OH + O2 = H2 + CHOCHO + CO2

      Free energy of reaction at 298 K is   -445.94 (kJ/mol)
        Enthalpy of reaction at 298 K is   -423.73 (kJ/mol)

***
  CHOCH:CH:OH + O2 = CHOCH2OH + CO2

      Free energy of reaction at 298 K is   -483.24 (kJ/mol)
        Enthalpy of reaction at 298 K is   -490.38 (kJ/mol)

```
***
  CHOCH:CH:OH +  O2 =  HCOOH +  CHOCHO

     Free energy of reaction at 298 K is     -402.54  (kJ/mol)
        Enthalpy of reaction at 298 K is     -408.83  (kJ/mol)

***
  CHOCH:CH:OH +  O2 =  CO2 +  OHCH:CH:OH

     Free energy of reaction at 298 K is     -440.32  (kJ/mol)
        Enthalpy of reaction at 298 K is     -439.81  (kJ/mol)

***
  CHOCH:CH:OH +  H2O =  CHO[OH]CHCH2OH

     Free energy of reaction at 298 K is        9.32  (kJ/mol)
        Enthalpy of reaction at 298 K is      -32.73  (kJ/mol)

***
  CHOCH:CH:OH +  H2O =  H2 +  CH2:CH:OH +  CO2

     Free energy of reaction at 298 K is      -67.08  (kJ/mol)
        Enthalpy of reaction at 298 K is      -37.37  (kJ/mol)

***
  CHOCH:CH:OH +  H2O =  H2 +  COOHCH:CH:OH

     Free energy of reaction at 298 K is      -15.59  (kJ/mol)
        Enthalpy of reaction at 298 K is      -22.69  (kJ/mol)

***
  CHOCH:CH:OH +  H2O =  CH2:CH:OH +  HCOOH

     Free energy of reaction at 298 K is      -23.68  (kJ/mol)
        Enthalpy of reaction at 298 K is      -22.47  (kJ/mol)

***

  Surviving species      9
              1      H2
              2      CHOCHO
              3      CO2
              4      CHOCH2OH
              5      HCOOH
              6      OHCH:CH:OH
              7      CHO[OH]CHCH2OH
              8      CH2:CH:OH
              9      COOHCH:CH:OH

Number of reactants      3
CHOCH2OH
O2
H2O
```

```
Radicals of component    CHOCH2OH                                    6
No. Radicals                      Valence Head     Radical   Radical
                                          position position-1 position-2
  1  H                              -1     T          1         0
  2  CHOCH                          -2     F          1         1
  3  CHOC                           -3     F          1         0
  4  COCH2OH                        -1     T          3         0
  5  CH2OH                          -1     T          2        ·0
  6  C                              -4     T          1         0


Radicals of component    O2                                          1
No. Radicals                      Valence Head     Radical   Radical
                                          position position-1 position-2
  1  O                              -2     T          1         1


Radicals of component    H2O                                         2
No. Radicals                      Valence Head     Radical   Radical
                                          position position-1 position-2
  1  H                              -1     T          1         0
  2  HO                             -1     T          2         0


New products          11
               1    H2
               2    O2
               3    H2O
               4    CHOCH2OH
               5    OHCH2OCH2OH
               6    CH3OH
               7    OHCH2CH2OH
               8    CHOCHO
               9    CO2
              10    COOHCH2OH
              11    CHOCOOH


Feasible reactions :

  CHOCH2OH +  O2 = 2 H2 + 2 CO2

     Free energy of reaction at 298 K is    -518.82  (kJ/mol)
        Enthalpy of reaction at 298 K is    -465.18  (kJ/mol)

***
  CHOCH2OH +  O2 =  H2O +  CHOCOOH

     Free energy of reaction at 298 K is    -435.89  (kJ/mol)
        Enthalpy of reaction at 298 K is    -440.04  (kJ/mol)

***
  CHOCH2OH +  H2O =  H2 +  CH3OH +  CO2

     Free energy of reaction at 298 K is     -74.70  (kJ/mol)
        Enthalpy of reaction at 298 K is     -45.58  (kJ/mol)
```
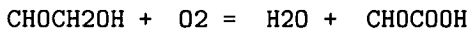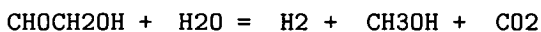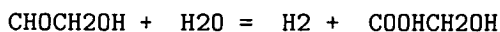
```
***
  CHOCH2OH +  H2O =  H2 +  COOHCH2OH


    Free energy of reaction at 298 K is     -15.59  (kJ/mol)
        Enthalpy of reaction at 298 K is     -22.69  (kJ/mol)


***

  Surviving species      6
             1      H2
             2      CO2
             3      H2O
             4      CHOCOOH
             5      CH3OH
             6      COOHCH2OH


Number of reactants      3
COOHCH2OH
O2
H2O


Radicals of component     COOHCH2OH                                5
No. Radicals                          Valence Head     Radical    Radical
                                              position position-1 position-2

  1  H                                   -1    T         1          0
  2  COOHCH                              -2    F         1          1
  3  COOHC                               -3    F         1          0
  4  CH2OH                               -1    T         2          0
  5  C                                   -4    T         1          0


Radicals of component     O2                                       1
No. Radicals                          Valence Head     Radical    Radical
                                              position position-1 position-2

  1  O                                   -2    T         1          1


Radicals of component     H2O                                      2
No. Radicals                          Valence Head     Radical    Radical
                                              position position-1 position-2

  1  H                                   -1    T         1          0
  2  HO                                  -1    T         2          0


New products              10
             1      H2
             2      O2
             3      H2O
             4      COOHCH2OH
             5      OHCH2OCH2OH
             6      CH3OH
             7      OHCH2CH2OH
             8      COOHCHO
             9      CO2
            10      COOHCOOH
```
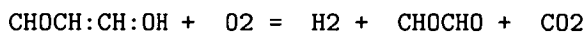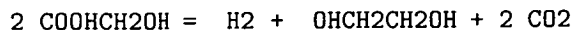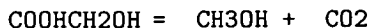
```
Feasible reactions :

2 COOHCH2OH =  H2 +  OHCH2CH2OH + 2 CO2

    Free energy of reaction at 298 K is    -67.34  (kJ/mol)
       Enthalpy of reaction at 298 K is     -2.45  (kJ/mol)


***
 COOHCH2OH =  CH3OH +  CO2

    Free energy of reaction at 298 K is    -59.11  (kJ/mol)
       Enthalpy of reaction at 298 K is    -22.89  (kJ/mol)


***
 COOHCH2OH +  O2 =  H2 +  H2O + 2 CO2

    Free energy of reaction at 298 K is   -503.23  (kJ/mol)
       Enthalpy of reaction at 298 K is   -442.49  (kJ/mol)


***
 COOHCH2OH +  O2 =  H2O +  COOHCOOH

    Free energy of reaction at 298 K is   -435.89  (kJ/mol)
       Enthalpy of reaction at 298 K is   -440.04  (kJ/mol)


***
 COOHCH2OH +  H2O = 3 H2 + 2 CO2    ·

    Free energy of reaction at 298 K is    -45.63  (kJ/mol)
       Enthalpy of reaction at 298 K is     41.51  (kJ/mol)


***

  Surviving species      6
            1      H2
            2      OHCH2CH2OH
            3      CO2
            4      CH3OH
            5      H2O
            6      COOHCOOH

Number of reactants      3
OHCH:CH:OH
O2
H2O


Radicals of component     OHCH:CH:OH                              5
No. Radicals                    Valence Head     Radical    Radical
                                        position position-1 position-2
  1  OHCHCHOH                      -2      F         2          3
  2  H                             -1      T         1          0
  3  CHOH                          -2      T         2          2
  4  CH:CH:                        -2      T         1          2
```
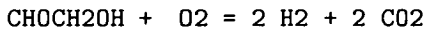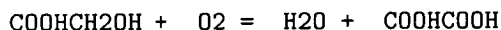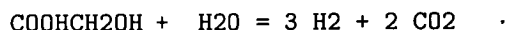
```
  5  OH                         -1      T        1          0
```

Radicals of component   O2   1

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

New products   6

```
             1     OHCH:CH:OH
             2     O2
             3     H2
             4     H2O
             5     OHCH:CH2:
             6     HCOOH
```

  Feasible reactions :

  OHCH:CH:OH + O2 = 2 HCOOH

    Free energy of reaction at 298 K is   -474.94 (kJ/mol)
       Enthalpy of reaction at 298 K is   -485.95 (kJ/mol)

  ***

  Surviving species   1
          1   HCOOH

Number of reactants   3
CH2O
O2
H2O

Atom decomposition of   CH2O   3

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1
2	C	-4	T	1	1
3	H	-1	T	1	0

Atom decomposition of   O2   1

No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Atom decomposition of   H2O   2

No. Radicals		Valence	Head position	Radical position-1	Radical position-2

```
1  O                            -2    T      1        1
2  H                            -1    T      1        0
```

New products   6
```
          1    O2
          2    CO2
          3    CO
          4    H2O
          5    CH4
          6    H2
```

Feasible reactions :

2 CH2O = CO2 + CH4

    Free energy of reaction at 298 K is   -225.47 (kJ/mol)
      Enthalpy of reaction at 298 K is   -236.70 (kJ/mol)

***
 CH2O = CO + H2

    Free energy of reaction at 298 K is   -27.40 (kJ/mol)
      Enthalpy of reaction at 298 K is   5.40 (kJ/mol)

***
 CH2O + O2 = CO2 + H2O

    Free energy of reaction at 298 K is   -513.40 (kJ/mol)
      Enthalpy of reaction at 298 K is   -519.80 (kJ/mol)

***
 CH2O + H2O = CO2 + 2 H2

    Free energy of reaction at 298 K is   -55.80 (kJ/mol)
      Enthalpy of reaction at 298 K is   -35.80 (kJ/mol)

***

 Surviving species   5
```
          1    CO2
          2    CH4
          3    CO
          4    H2
          5    H2O
```

Number of reactants   3
OHCH2CH3
O2
H2O

Radicals of component   OHCH2CH3   3

No. Radicals	Valence	Head position	Radical position-1	Radical position-2

```
 1  H                                 -1       T       1          0
 2  CHCH3                             -2       T       2          2
 3  CCH3                              -3       T       2          0
```

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

```
New products            6
              1     H2
              2     O2
              3     H2O
              4     OHCH2CH3
              5     CHOCH3
              6     COOHCH3
```

Feasible reactions :
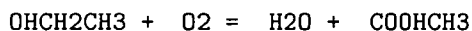
OHCH2CH3 + O2 = H2O + COOHCH3

```
    Free energy of reaction at 298 K is     -435.89   (kJ/mol)
       Enthalpy of reaction at 298 K is     -440.04   (kJ/mol)
```

***

```
  Surviving species      2
            1     H2O
            2     COOHCH3
```

```
Number of reactants     3
CH3OH
O2
H2O
```

Radicals of component   CH3OH   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 CH2	-2	F	1	1

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   5

1	H2
2	O2
3	H2O
4	CH3OH
5	CH2O

Feasible reactions :

   Surviving species   0

Number of reactants   3
COOHCH2CH3
O2
H2O

Radicals of component   COOHCH2CH3   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 CH2CH3	-1	T	2	0
2 C	-4	T	1	0

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	2	0

New products   7

1	O2
2	CH3CH3
3	H2
4	H2O
5	CH3CH2CH2CH3
6	CO2
7	OHCH2CH3

Feasible reactions :
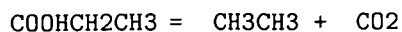
   COOHCH2CH3 = CH3CH3 + CO2

```
      Free energy of reaction at 298 K is     -59.11  (kJ/mol)
         Enthalpy of reaction at 298 K is     -22.89  (kJ/mol)


***
2 COOHCH2CH3 =  H2 +  CH3CH2CH2CH3 + 2 CO2

      Free energy of reaction at 298 K is     -67.34  (kJ/mol)
         Enthalpy of reaction at 298 K is      -2.45  (kJ/mol)


***

  Surviving species      4
            1      CH3CH3
            2      CO2
            3      H2
            4      CH3CH2CH2CH3


Number of reactants      3
CH3OH
O2
H2O
```

Radicals of component   CH3OH   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 CH2	-2	F	1	1

Radicals of component   O2   1

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 O	-2	T	1	1

Radicals of component   H2O   2

No. Radicals	Valence	Head position	Radical position-1	Radical position-2
1 H	-1	T	1	0
2 HO	-1	T	· 2	0

```
New products            5
            1      H2
            2      O2
            3      H2O
            4      CH3OH
            5      CH2O



  Feasible reactions :


  Surviving species      0

Number of reactants      3
{OH}C6H4CH2CH2OH
```
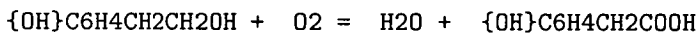
```
O2
H2O
```

Radicals of component   {OH}C6H4CH2CH2OH   3

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	{OH}C6H4CH2CH	-2	F	1	1
3	{OH}C6H4CH2C	-3	F	1	0

Radicals of component   O2   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	O	-2	T	1	1

Radicals of component   H2O   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	HO	-1	T	2	0

```
New products          6
              1     H2
              2     O2
              3     H2O
              4     {OH}C6H4CH2CH2OH
              5     {OH}C6H4CH2CHO
              6     {OH}C6H4CH2COOH
```

Feasible reactions :

```
  {OH}C6H4CH2CH2OH  +  O2  =  H2O  +  {OH}C6H4CH2COOH

    Free energy of reaction at 298 K is    -435.89   (kJ/mol)
       Enthalpy of reaction at 298 K is    -440.04   (kJ/mol)
```

***

```
  Surviving species      2
          1     H2O
          2     {OH}C6H4CH2COOH
```

```
Number of reactants      3
{OH}C6H4CH2COOH
O2
H2O
```

Radicals of component   {OH}C6H4CH2COOH   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	{OH}C6H4CH2	-1	F	1	0
2	C	-4	T	1	0

Radicals of component	O2			1
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 O		-2	T	1	1

Radicals of component	H2O			2
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 H		-1	T	1	0
2 HO		-1	T	2	0

New products   6
          1   O2
          2   {OH}C6H4CH3
          3   H2
          4   H2O
          5   CO2
          6   {OH}C6H4CH2OH

Feasible reactions :

  {OH}C6H4CH2COOH = {OH}C6H4CH3 + CO2

    Free energy of reaction at 298 K is   -59.11 (kJ/mol)
      Enthalpy of reaction at 298 K is   -22.89 (kJ/mol)

 ***

  Surviving species   2
          1   {OH}C6H4CH3
          2   CO2

Number of reactants   3
{OH}C6H4COCH3
O2
H2O

Radicals of component	{OH}C6H4COCH3			0
No. Radicals		Valence	Head position	Radical position-1	Radical position-2

Radicals of component	O2			1
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 O		-2	T	1	1

Radicals of component	H2O			2
No. Radicals		Valence	Head position	Radical position-1	Radical position-2
1 H		-1	T	1	0
2 HO		-1	T	2	0

New products   3

```
            1      H2
            2      02
            3      H20
```

Feasible reactions :

  Surviving species   0

Number of reactants   3
{OH}C6H4CH3
02
H20

Radicals of component   {OH}C6H4CH3   .   16

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	F	1	0
2	{OH}C6H4CH2	-1	F	1	1
3	CH3	-1	T	1	0
4	{OH}C6H4	-1	F	1	0
5	CH2:CH:CH:CH:CHCH2	-2	F	1	2
6	CH2	-2	T	1	1
7	CH2:CH:CH:CH:CH	-2	F	1	1
8	CH:CH:CH:CH:	-2	T	1	4
9	CH:CH:	-2	T	1	2
10	CHCH	-4	F	1	2
11	CH2:CH:CHCHCH:CH2:	-2	F	3	4
12	CHCH:CH2:	-2	T	3	3
13	CH3CCH	-4	F	1	2
14	CH2CH:CH:CH:CH:CH2	-2	F	1	6
15	COCH:CH:CH:CH:CO	-2	F	1	6
16	CHCOCH:CH:COCH	-4	F	1	6

Radicals of component   02   1

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	0	-2	T	1	1

Radicals of component   H20   2

No.	Radicals	Valence	Head position	Radical position-1	Radical position-2
1	H	-1	T	1	0
2	H0	-1	T	2	0

New products   31

```
            1      H2
            2      02
            3      H20
            4      {OH}C6H4CH3
            5      CH4
            6      {OH}C6H5
            7      CH2:CH:CH:CH:CH:CH2:
```

```
 8     CH3OH
 9     OHCH:CH:CH:CH2:
10     OHCH:CH2:
11     OHCH2CH2OH
12     OHCH2CH:CH2:
13     CH3CH3
14     CHOCH:CH:CH:CH:CHO
15     CH2O
16     CHOCHO
17     CHOCH:CH2:
18     CH3COCHO
19     CHOCOCH:CH:COCHO
20     {OH}C6H4CH2OH
21     {OH}C6H4{OH}
22     OHCH:CH:CH:CH:OH
23     OHCH:CH:OH
24     OHCH2CH:CH:CH:CH:CH2OH
25     COOHCH:CH:CH:CH:COOH
26     OHCH2CH:CH:CH:CH:CH3
27     COOHCH:CH:CH:CH:CHO
28     CH3[OH]CHCH2OH
29     OHCH2CHO
30     CH3[OH]CHCHO
31     OHCH2COCH:CH:COCHO
```
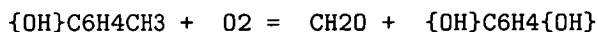
Feasible reactions :

 {OH}C6H4CH3 + O2 = CHOCH:CH:CH:CH:CHO + CH2O

    Free energy of reaction at 298 K is   -114.81 (kJ/mol)
       Enthalpy of reaction at 298 K is   -91.30 (kJ/mol)
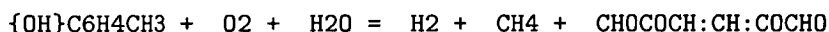
***
 {OH}C6H4CH3 + O2 = CH2O + {OH}C6H4{OH}

    Free energy of reaction at 298 K is   -263.41 (kJ/mol)
       Enthalpy of reaction at 298 K is   -261.20 (kJ/mol)

***
 {OH}C6H4CH3 + O2 + H2O = H2 + CH4 + CHOCOCH:CH:COCHO

    Free energy of reaction at 298 K is   -164.94 (kJ/mol)
       Enthalpy of reaction at 298 K is   -150.58 (kJ/mol)

***
 {OH}C6H4CH3 + O2 + H2O = H2 + CH2O + COOHCH:CH:CH:CH:CHO
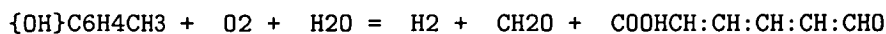
    Free energy of reaction at 298 K is   -130.40 (kJ/mol)
       Enthalpy of reaction at 298 K is   -113.99 (kJ/mol)

***
 {OH}C6H4CH3 + O2 + H2O = CH4 + COOHCH:CH:CH:CH:COOH
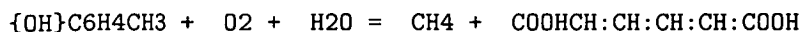
```
    Free energy of reaction at 298 K is    -315.66  (kJ/mol)
       Enthalpy of reaction at 298 K is    -337.58  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  CH4 +  OHCH2COCH:CH:COCHO

    Free energy of reaction at 298 K is    -202.24  (kJ/mol)
       Enthalpy of reaction at 298 K is    -217.23  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  CH3OH +  COOHCH:CH:CH:CH:CHO

    Free energy of reaction at 298 K is    -199.68  (kJ/mol)
       Enthalpy of reaction at 298 K is    -214.19  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  OHCH:CH:CH:CH2: +  CH2O +  CHOCHO

    Free energy of reaction at 298 K is     -66.09  (kJ/mol)
       Enthalpy of reaction at 298 K is     -36.65  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  OHCH:CH2: +  CHOCHO +  CHOCH:CH2:

    Free energy of reaction at 298 K is     -90.45  (kJ/mol)
       Enthalpy of reaction at 298 K is     -61.99  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  CH2O +  CHOCH:CH2: +  CH3COCHO

    Free energy of reaction at 298 K is    -138.41  (kJ/mol)
       Enthalpy of reaction at 298 K is    -114.22  (kJ/mol)


***
 {OH}C6H4CH3 +  O2 +  H2O =  CH3COCHO +  OHCH:CH:CH:CH:OH

    Free energy of reaction at 298 K is    -121.51  (kJ/mol)
       Enthalpy of reaction at 298 K is    -128.73  (kJ/mol)


***

 Surviving species    16
           1      CHOCH:CH:CH:CH:CHO
           2      CH2O
           3      {OH}C6H4{OH}
           4      H2
           5      CH4
           6      CHOCOCH:CH:COCHO
           7      COOHCH:CH:CH:CH:CHO
           8      COOHCH:CH:CH:CH:COOH
           9      OHCH2COCH:CH:COCHO
          10      CH3OH
          11      OHCH:CH:CH:CH2:
          12      CHOCHO
```
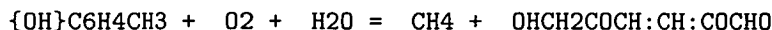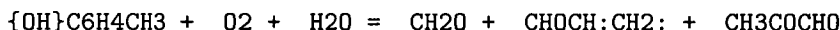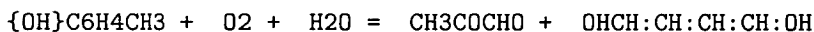
```
13      OHCH:CH2:
14      CHOCH:CH2:
15      CH3COCHO
16      OHCH:CH:CH:CH:OH
```